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ON THE ANALYTIC SOLUTION OF THE
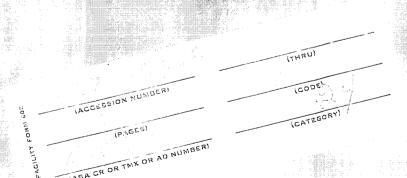
SCHRÖDINGER EQUATION FOR THE TWO-ELECTRON ATOM

by

Ronald Joseph White

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SCHRÖDINGER EQUATION FOR THE TWO-ELECTRON ATOM[*]

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ABSTRACT

The Schrödinger equation for the ground state of the two-electron atom is examined in detail and a technique is introduced by means of which an analytic solution may be realized. The technique, which may be called a partial series expansion method, consists of assuming a series form for the wavefunction in powers of the inter-electron separation with coefficients which are functions of two variables and of determining the coefficients so that a satisfactory solution of the Schrödinger equation results. The coefficients are related by first-order differential recursion relations which may be integrated explicitly. The method is not complete because the initial coefficient, independent of the inter-electron separation, is undetermined. The extension of the method to the hydrogen molecule and the two-electron atom in the presence of a uniform electric field is also considered. Two model atomic systems, the Hooke's law model and the delta-function model, for the two-electron atom are also discussed and it is shown that these systems, which are solvable through first order in a perturbation series, yield information about the difficulties which arise in the helium atom.

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Acknowledgement

As is the case with most students nearing the end of a graduate career and faced with the responsibility of publicly acknowledging that the difficulties encountered were not surmounted through their own efforts, I must admit that I hardly know where to begin. Borrowing a technical wording, let me say that the following is not intended to be an exhaustive survey of all who have contributed to the writing of this thesis, rather it is only a guide to the directions of my inadequacies.

I wish to thank Professor William Byers Brown for his encouragement, advice, and personal demonstration of the scientific method as well as for his inexhaustible supply of new ideas just when the hour was darkest;

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My co-workers and companions Dr. Tai Yup Chang, Dr. Russell

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I. INTRODUCTION

For over forty years, ever since the birth of modern quantum mechanics, the analytical solution of the Schrödinger equation for the two-electron atom has eluded those in its quest. It was recognized very quickly that the problem was a non-separable one and experience in other fields had shown that non-separable problems were not amenable to exact treatment except in certain special cases.[1] Since it was the two-electron atom which had brought to the fore the inadequacies of the "old quantum theory" it was realized that a satisfactory treatment of helium was the first crucial test which any new theory must pass.

With a certain sense of relief it was found that even the earliest attempts[2,10] at an approximate solution for the ground state met with reasonable success. Today, with modern computational equipment readily available, it is possible to obtain approximate solutions which yield energy values accurate[3] to the same degree as spectroscopic measurements. The two-electron atom has often served as the testing ground or starting point of approximate calculations aimed at larger less tractable atomic and molecular systems. Of late, it has proved possible to obtain mass polarization, relativistic, and Lamb shift corrections to the ground state energy with high accuracy[4] providing a check on quantum electrodynamic theories of electron interaction. Indeed, the importance of the two-electron system in modern quantum mechanics needs little emphasis.

The success of methods directed at obtaining analytic solutions has been somewhat less spectacular than those which have sought good approximations. Even the form of such solutions is in some doubt. In fact, for twenty-two years the existence of solutions was never proved[5].

The purpose of this work is to present a critical survey of the past efforts to obtain analytical solutions and to introduce a new approach by means of which an analytical solution may be realized. Although a great deal of the past work on approximate solutions will be mentioned, this thesis is not intended to be an exhaustive review of the subject[6]. The following pages will concern only the non-relativistic, electrostatic Schrödinger equation for two electrons moving in the field of a fixed nucleus of charge Z . Only the ground state will be discussed here[7]. Whenever any energy eigenvalues are given they will concern only the case Z=2, the He atom. Spin-orbit interaction will be ignored and it will be assumed that the spin has been removed from the problem.

Using conventional atomic units (energy measured in Hartrees, H; length measured in Bohrs, B) the Schrödinger equation is

$$(H - E)\Psi(\vec{r}_1, \vec{r}_2) = 0 \qquad (1)$$

where

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \, .$$

The vectors $\vec{r}_1$, $\vec{r}_2$ and $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$ specify the positions of the electrons with respect to the nucleus and to each other, while ∇_i^2 is the Laplacian operator in the space of the i'th electron.

For the ground state Ψ is a function of only three variables[8] which specify the shape of the electron-electron-nucleus triangle and Ψ must be symmetric with respect to interchange of the labels on electrons 1 and 2. The ground state is thus a para-state.

The plan of this thesis is as follows: Section II presents an historical survey of the past attempts to solve the helium problem and is divided into three parts: Section II.1 examines the variational approach, section II.2 the perturbation-variation approach and section II.3 the direct approach through the analysis of the differential equations. Section III presents a technique by means of which an exact solution of a wide class of two-electron problems may be realized. Section III.1 treats the Hooke's law model of the two-electron atom while section III.2 examines the delta function model for such a system. Section III.3 is concerned with the solution of the first-order perturbation equation which arises in Z^{-1} perturbation theory for helium. Section III.4 treats the total non-relativistic equation for the two-electron atom in an analogous manner, and in sections III.5 and III.6 this analysis is extended to the two-electron diatomic molecule, hydrogen, and to the two-electron atom in the presence of a uniform electric field.

The author's original contributions are (1) the discovery of

the beautiful and relatively simple first-order differential recursion relations which occur in a one variable (r_{12}) power series expansion of the wave function for a wide class of two-electron problems (section III), (2) the refutation of Bartlett's argument for the existence of certain logarithmic terms in the helium wave function (Appendix F), (3) the consideration of the boundary conditions imposed by the hermiticity of the Hamiltonian when using Hylleraas coordinates (Appendix H), and (4) the treatment of the Hooke's law model for the two-electron atom (Appended report, Appendix E, and section III.1).

An investigation has also been carried out by the author into the possibility of finding four-particle perimetric coordinates and this is included as Appendix D.

II.   A CRITICAL HISTORICAL SURVEY

In attempting to solve an eigenvalue problem like equation (I.1) several alternative methods of attack are possible and almost every technique has been investigated to some extent using the two-electron atom.   In spite of the wide variety of the approaches, it is possible to classify almost all of them under three broad headings.   These three main arteries which have led to the elucidation of much information about the solution of equation (I.1) are

1. The Variational Technique,

2. The Perturbation-variation Technique, and

3. The Direct Approach via the differential equations.

An examination of these main avenues and their many variants will now be made.   The study of the third or direct approach will be more detailed since the first two techniques are probably more familiar.

1. The Variational Technique

Every student of elementary quantum mechanics is taught the
power of using a variational approach in order to obtain approximate
solutions to the Schrödinger equation. Appendix A contains the main
elements of the variational technique needed to understand the
following. In Appendix B a discussion of the coordinate systems
used to study equation (I.1) is given.

Tables 1 and 2 contain a summary of the results obtained by
this technique for helium.

The earliest successful attempts[9] at a description of the
wavefunction for He were rather crude, but served to indicate that
a description of experiment was possible. Indeed, Kellner's result[2]
of -2.847656 for the ground state energy (using scaled hydrogenic
functions) accounted for 98.1 % of the true value. Hylleraas took
the problem in hand[10,11,12,13] and pushed the theoretical results
into almost complete agreement with the experimental evidence of
the times. He realized that the wavefunction must depend on three
variables and that the chief reason for the inaccuracy in the
previous attempts was the absence of the third variable. Hylleraas
saw that there were essentially two paths open: 1) the introduction
of the third variable as an angle (see equation (B.2)), or 2) the
introduction of the third variable as a length (see equation B.3)).
He found that the first choice was not well-suited to rapid

convergence[10], but that the second was extremely well adapted[12] to the task at hand. The first choice has since become known as the method of superposition of configurations, while the second method may be termed the direct r_{ij} method. The culmination of Hylleraas's early work on helium was the introduction of a six parameter wave function[12] which was to remain the best approximate wave function available for twenty-four years. The eigenvalue he obtained, -2.90324, is in error only by 0.016%.

Hylleraas's calculation was extremely important in that it demonstrated that the existing formulation of quantum mechanics was capable of reproducing experimental results on a system with more than one electron[14]. It was only after this had been proved that wide acceptance of the formulation of quantum mechanics was gained.

Hartree[15] and Fock[16] approached the problem in a little different way. Rather than merely inserting parameters into a trial function and determining the best values of these parameters by the variational theorem, they sought to determine entire functions by minimization of the energy. If a trial function of the form

$$\psi_{HF} = \phi(r_1) \phi(r_2) \tag{1}$$

is used and if the variation of the energy integral is carried out with respect to arbitrary variation in ϕ, then the equation which determines ϕ is

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{z}{r_1} + \int d\gamma_2 \frac{\phi^2(r_2)}{r_{12}} - \epsilon \right] \phi(r_1) = 0 \qquad (2)$$

with corresponding energy

$$\tilde{E} = 2\epsilon - \left\langle \psi_{HF}, \frac{1}{r_{12}} \psi_{HF} \right\rangle . \qquad (3)$$

This equation, which determines both the best wavefunction of the form given by equation (1) and the best energy associated with this form, may be solved numerically[17], by perturbation theory[18,19], or by assuming a form for ϕ with variable parameters and iterating until self-consistent values of the parameters are obtained[20]. The energy obtained by this procedure, -2.86167, does not compete with a Hylleraas type variational calculation, but the extension of this technique to larger systems is straightforward and has yielded much important information on many electron atoms[21]. The error in the energy in this calculation is called the correlation energy[22] since the Hartree-Fock approximation only takes into consideration the motion of each electron in the average field of the other and does not consider specific correlation between the motion of the electrons. The recent concepts of the natural spin orbitals[23], and extended Hartree-Fock theory[24] (different orbitals for different spins) are important, but their detailed study is beyond the scope of this thesis. Table 2 does contain some results of these techniques for the ground state.

The variational theorem provides only upper bounds to the energy. Several workers[25,26] have attempted to obtain lower bounds which, for the ground state at least, would agree with the upper bound calculations to within experimental accuracy. No such complete agreement was found and the problem of finding good lower bounds for the energy eigenvalue is still not completely solved[27]. The present state of the work on lower bounds is summarized in Appendix C.

The fifties saw a new awakening of interest in the problem of the two electron atom, and the improvement in computational facilities greatly extended the capability of the researcher. The method of superposition of configurations drew renewed interest[28,29] because this method of introducing correlation between the motion of the two electrons was more easily extended to larger systems than the direct introduction of metric variables and also because it was not understood why the method converged so slowly. More details concerning this technique are considered at the end of this section and there the reason for the slow convergence will become clear.

Numerous investigators[30,31] also considered the problem by introducing a third metric variable as Hylleraas had done. Only now, guided by theory, various coordinate systems (see Appendix B) and various unconventional terms (half-integral powers,[32,33] logarithmic terms,[3,34,35] negative power terms[25,36]) were tried in large variational treatments. One of the most interesting of the new coordinate systems to be tried is the perimetric coordinates used by Pekeris.[37,38] Perimetric coordinates have the property

that each coordinate has the independent range $(0, \infty)$. Thus, if
the trial wavefunction is expanded in terms of a complete set
consisting of a product of three Laguerre Polynomials with
appropriate weight factor, the recurrence relations between the
Laguerre Polynomials and their   orthonormality property permit
the evaluation of all matrix elements in a simple way. The infinite
secular equation, which is then truncated, consists of a sparse
determinant of easily obtained elements. These properties allowed
Pekeris to consider a determinant of order 1078[38].

The extension of this technique to larger atoms[39,40] would
have permitted very exact calculations in a simple manner. It has
been proved, however that extension is not possible[41,42]. The
author's contribution to this effort is contained in Appendix D.

Today the best variational calculational on the ground state
of helium is that of Frankowski and Pekeris[3]. Using logarithmic
and half-integral terms they obtained the result -2.9037243770326
with a determinant of order 246.

2. The Perturbation-variation Technique

Concurrent with his early success using a strict variational approach to obtain an approximate solution of equation (I.1), E. A. Hylleraas introduced and applied perturbation theory[13] to the two-electron atom. At first, and for over twenty-five years thereafter, perturbation theory was considered useful only for atoms of large Z[43]. It was thought of, by Hylleraas himself, only as a theoretical guide[44] to be used for interpolation purposes. Within the last few years, however, the technique has come to be regarded as one of the most powerful practical means at the disposal of the researcher. As there have been several recent reviews on the subject,[45,46] the treatment presented here is intended to serve mainly as a guide to notation.

It has been proposed[47] to call the perturbation approach described here the Hylleraas-Scherr-Knight (HSK) variational perturbation method. The notation used here is that introduced by Scherr and Knight[48,49,50] and more details on the method are presented in their work.

If the units in equation (I.1) are changed to Z-reduced units (energy in Z^2 Hartrees, length in Z Bohrs) the Schrödinger equation for the two-electron atom becomes

$$(H_0 + \lambda V - E)\, \Psi = 0 \tag{4}$$

where

$$H_0 = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_1} - \frac{1}{r_2} ,$$

$$V = \frac{1}{r_{12}} , \tag{5}$$

$$\lambda = \frac{1}{Z} .$$

The parameter $\lambda = Z^{-1}$ thus becomes a "natural perturbation parameter" and the assumption that Ψ and E are analytic functions of this parameter

$$\Psi = \sum_{n=0}^{\infty} \lambda^n \psi_n , \tag{6}$$

$$E = \sum_{n=0}^{\infty} \lambda^n \epsilon_n \tag{7}$$

leads, after substitution of equations (6) and (7) into equation (4), to an infinite set of coupled equations for the ψ_n and ϵ_n,

$$(H_0 - \epsilon_0)\psi_n + (V - \epsilon_1)\psi_{n-1} - \sum_{k=2}^{n} \epsilon_k \psi_{n-k} = 0 \tag{8}$$

where terms in equation (8) with negative indices are to be ignored.

The first equation in this series is an eigenvalue equation

$$(H_0 - \epsilon_0)\psi_0 = 0 \tag{9}$$

whose ground state solution is

$$\psi_0 = \pi^{-1} \exp(-r_1 - r_2),$$

$$\epsilon_0 = -1. \tag{10}$$

The remaining equations are inhomogeneous partial differential equations whose exact solutions are difficult to obtain. Approximate solutions may be obtained in the following way. A trial wave function is employed having the form

$$\psi = \psi_0 + \sum_{n=1}^{\infty} \lambda^n \varphi_n \tag{11}$$

where the φ_n are chosen from some finite auxiliary set

$$\varphi_m = \sum_{i=1}^{m} C_{m,i} N_i . \tag{12}$$

Insertion of equations (11) and (7) into the variational theorem, equation (A.3), leads to the following set of equations

$$\langle \varphi_m, (H_0 - \epsilon_0) \varphi_m \rangle + 2 \langle \varphi_m, (V - \epsilon_1) \varphi_{m-1} \rangle$$

$$- \sum_{p=2}^{2m-1} \epsilon_p \sum_{i=m-p}^{m} \langle \varphi_i, \varphi_{2m-p-i} \rangle \geqslant \epsilon_{2m} \langle \psi_0, \psi_0 \rangle,$$

$$m = 1, 2, \cdots \tag{13}$$

where negative indices are to be ignored and where φ_p, ϵ_{2p} and

ϵ_{2p+1} p=0,1,2,...,n-1 have already been sufficiently exactly

determined. This, then, is a variational equation which may used

to determine φ_m . ϵ_{2n+1} may be calculated by the equation

$$\epsilon_{2n+1} \langle \psi_0, \psi_0 \rangle = \langle \varphi_n, (V - \epsilon_1) \varphi_n \rangle \qquad (14)$$
$$- \sum_{p=2}^{2m} \epsilon_p \sum_{i=n-p+1}^{n} \langle \varphi_i, \varphi_{2n+1-p-i} \rangle$$

Hylleraas's early calculations were concerned with obtaining

an approximate first order[13] wave function, but Scherr and Knight

realized that higher order calculations were fairly simple to obtain

using a computer and they calculated an approximate sixth order[50]

wavefunction. Midtdal has since published a calculation to twenty-

first order[47] in the energy (tenth order in the wave function) and

has some results to mkch higher orders[4]. Table 4 gives the energy

coefficients available. In their calculations Scherr and Knight

used a basis set (v_i in equation (12)) consisting of 100 terms of

Kinoshita type while Midtdal used up to 204 terms of Hylleraas type.

(See Appendix B for nomenclature on type of terms.)

There are many facets of this perturbation treatment which are

still in the forefront of research and it is impossible to consider

them all here. One interesting study concerns the radius of

convergence of the perturbation series for the energy, equation (7).

It is known that this series converges[51] for small enough λ and

that the radius of convergence is finite, but the position and type

of singularity nearest the origin is not known. Stillinger[52], using

Midtdal's results, has tentatively characterized the singularity as

a branch point on the real λ axis at $\lambda^* = 1.1184$ of approximate

order 6/5 (1.2057). Midtdal, however, mentions[53] that oscillations

set in at higher order which destroy the regular nature of the

energy coefficients and it may require more investigation to

determine whether or not this is caused by the finite basis set

used. Midtdal estimates the position of the singularity at

$\lambda^* \simeq 1.22$. Clearly the question of the radius of convergence

remains open, but it seems safe to conclude that the series converges

for all systems of interest, $Z \geq 1$.

Perturbation theory has been used in other ways to study the

two-electron atom. Byers Brown and Nazaroff[54] discuss the perturba-

tion theory of the correlation orbital. The solution to the Hartree-

Fock equation[18,19] equation (2), may be approached using the

technique of perturbation theory. Byron and Joachain[55,56] have used

the Hartree-Fock wavefunction as the zeroth order approximation

(instead of the hydrogenic ψ_0 in equation (10)) and have calculated

the energy to fifth order. Their results are given in Table 5.

Here the perturbation parameter is equal to unity.

Byron and Joachain[56] also present an extensive calculation of

the superposition of configuration type for the first order wave

function and the second order energy in Z^{-1} perturbation theory.

The first order equation (cf. equation (8)) is

$$(H_0 - \epsilon_0)\psi_1 + (V - \epsilon_1)\psi_0 = 0 \tag{15}$$

where ψ_0 is given by equation (10). The variational principle

for ψ_1 (equation (13) with $n = 1$) is then used with trial

functions of the type

$$\psi_1 = \sum_{\ell=0}^{\infty} \phi_\ell (r_1, r_2) P_\ell (\cos\theta) \tag{16}$$

where various forms with embedded parameters are used for the ϕ_ℓ.

The second order energy can be put into a corresponding form[57]

$$\epsilon_2 = \sum_{\ell=0}^{\infty} \epsilon_2(\ell) . \tag{17}$$

Byron and Joachain's calculation was continued through $\ell = 20$, and

the resulting $\epsilon_2(\ell)$ to $\ell = 10$ are given in Table 6. In Appendix E

it is demonstrated that the asymptotic form of $\epsilon_2(\ell)$ for large ℓ

should be

$$\epsilon_2(\ell) = -\frac{45}{256}(\ell+\tfrac{1}{2})^{-4}\left[1 - \frac{5}{4}(\ell+\tfrac{1}{2})^{-2} + O(\ell^{-4})\right]. \tag{18}$$

This asymptotic formula gives

$$\epsilon_2(20) = -0.992 \times 10^{-6} \tag{19}$$

while Byron and Joachain's variational results give

$$\epsilon_2(20) = -0.944 \times 10^{-6}$$

(20)

which is reasonable agreement.

This calculation demonstrates the slow convergence inherent in all superposition of configuration calculations. The coulombic repulsive potential between the electrons causes the energy associated with the P_ℓ component of the wave function to behave like ℓ^{-4}. Thus, many ℓ values must be included if extremely exact results are required. On the other hand, moderate accuracy is relatively easy to obtain. Although the argument given here is for the first order wave function, similar reasoning applies to total wave function.[58]

3. The Direct Approach via the Differential Equations

Direct attempts to study the Schrödinger equation for the two-electron atom have not, in general, enjoyed the success of the variational type calculation. This is mainly due to the non-separability of the equation and the corresponding lack of any definite scheme for the development of acceptable solutions. The earliest work in this direction was by Gronwall[59,60]. However, he died before he was able to achieve any concrete results. Bartlett[61,62] was the first to make a statement about the actual form of the wave-function, but his work is essentially of a negative nature in that he showed what type of function could not be a solution of the Schrödinger equation for helium. Bartlett[62] also purports to show that a certain type of logarithmic term must appear in the true solution, but it is shown in Appendix F that his analysis is incorrect in this respect. Kato,[5,51,64,65] abandoning this type of analysis, was able to prove a number of general theorems by resorting to the abstract theory of operators in Hilbert space. In particular, he was able to show rigorously that the wave equation for the two-electron atom possesses a solution for the ground state. Fock[66] was able to characterize the solution as being of a certain type containing logarithmic terms (which were of a different type than those mentioned previously by Bartlett), but was not able to realize a complete solution because of computational difficulties. Kinoshita[36] considered series solutions in more detail and showed that a certain type of series could yield a formal solution to the

equation, but that such solutions did not appear easily realizable. Munschy and Pluvinage[67] also attempted a series solution but were unable to overcome the computational difficulties.

Kato's Results

Kato's results[5,64,65] solidify the ground on which much of what follows rests and will be summarized first. Kato proved

1. That the Hamiltonian operator H of equation (I.1) is essentially self-adjoint when restricted to functions in a certain domain $\mathcal{D}_0$.

2. That the domain $\mathcal{D}_0$ on which H is defined is completely characterized by the following boundary conditions in terms of the momentum representation

$$\iint |F(\vec{p}_1, \vec{p}_2)|^2 \, d\vec{p}_1 \, d\vec{p}_2 < \infty, \qquad (21)$$

$$\iint p_i^4 |F(\vec{p}_1, \vec{p}_2)|^2 \, d\vec{p}_1 \, d\vec{p}_2 < \infty, \qquad (22)$$
$$i = 1,2 .$$

3. That the eigenfunctions of this Hamiltonian operator exist.

4. That the eigenfunctions are continuous and analytic, satisfy the wave equation everywhere except possibly at singular points of the potential, and possess derivatives of first order which are bounded everywhere.

5. That the following relations hold at the Coulomb singular

points (in atomic units)

$$\frac{\partial \Psi}{\partial r_{12}}\Bigg|_{r_{12}=0} = \frac{1}{2}\Psi(r_{12}=0) , \qquad (23)$$

$$\left(\frac{\partial \hat{\Psi}}{\partial r_{\lambda}}\right)_{r_{j}}\Bigg|_{r_{\lambda}=0} = -Z\Psi(r_{\lambda}=0) , \qquad (24)$$

$$\lambda, j = 1,2$$

where $\hat{\Psi}$ is the average of Ψ over a small sphere

about the singular point $r_{\lambda}=0$.

The characterization of the domain of H in the momentum

representation is clear and concise but not very convenient for a

study of the differential equations in configuration space. The

proper boundary conditions which characterize this domain in any

set of coordinates in configuration space are difficult to formulate.

Roughly speaking, however, the following conditions are necessary

to characterize the domain

$$\langle \Psi, \Psi \rangle < \infty , \qquad (25)$$

$$\langle (\nabla_1^2 + \nabla_2^2)\Psi, (\nabla_1^2 + \nabla_2^2)\Psi \rangle < \infty , \qquad (26)$$

and

$$\langle \Psi, (\nabla_1^2 + \nabla_2^2)\, \Phi \rangle = \langle (\nabla_1^2 + \nabla_2^2)\Psi, \Phi \rangle \tag{27}$$

for all Φ and Ψ contained in $\mathcal{D}_0$.

The words "roughly speaking" at the beginning of the last sentence were necessary because a function Ψ need not be differentiable everywhere, but only need have generalized derivatives up to the second order which are square integrable[68]. The generalized derivative is the inverse Fourier transform of multiplication by the corresponding momentum variable in momentum space. If the functions being considered are smooth enough the generalized derivative is equivalent to the ordinary derivative and that will be assumed in what follows.

Equation (27) merely states the fact that Green's theorem is to be valid for functions in the domain $\mathcal{D}_0$. In certain coordinate systems, e.g. cartesian coordinates, the validity of Green's theorem follows directly from equations (25) and (26), but in other cases this is not so. Integration by parts of one side of equation (27) leads to certain boundary terms which must vanish for all Ψ and Φ in the domain $\mathcal{D}_0$. These boundary terms are sometimes very unwieldy, especially in coordinate systems which do not have independent ranges such as the Hylleraas coordinates s,t,u. Nevertheless these conditions can always be obtained explicitly by an integration by parts. Appendix H gives the conditions explicitly

for the Hylleraas coordinates s,t,u.

Notice that the boundary conditions given by equations (25), (26), and (27) are a bit stronger than the conditions usually associated with the variational approach to the problem. Even if cartesian coordinates are considered so that equation (27) follows directly from (25) and (26), there is a difference between the two approaches. The conditions required by the variational principle, if the potential is coulombic, are that

$$\langle \Psi, \Psi \rangle < \infty , \tag{28}$$

and

$$\langle \Psi, T\Psi \rangle < \infty \tag{29}$$

where T is the kinetic energy operator. Equations (25) is identical to equation (28), but equation (26) is equivalent to

$$\langle T\Psi, T\Psi \rangle < \infty . \tag{30}$$

This latter requirement is stronger than that of equation (29). The situation seems a bit strange, but the above implies that the variation is carried out with respect to a wider class of functions (those which satisfy equation (29) and then if the extremum is obtained for the variational integral the resulting Ψ will satisfy

the stronger requirement, equation (30).

Fock's Method

Fock[66] approached the two-electron problem in a more traditional way and discovered that the wavefunction must have a certain form which contains logarithmic terms. If the equation for the two-electron atom is written in Z-reduced atomic units and if perturbation theory is applied to the equation, as in equations (4) through (10), the equation which determines the first order correction to the zeroth order wavefunction given by equation (10) is

$$(H_0 - \epsilon_0)\psi_1 = \left(\epsilon_1 - \frac{1}{r_{12}}\right)\psi_0 \tag{31}$$

where

$$\psi_0 = \pi^{-1} \exp(-r_1 - r_2),$$

$$\epsilon_0 = -1, \tag{32}$$

$$\epsilon_1 = \frac{5}{8}.$$

If the variables used are those introduced by Fock (see Appendix B)

$$\rho^2 = r_1^2 + r_2^2,$$

$$\tan \frac{\alpha}{2} = \frac{r_2}{r_1}, \tag{33}$$

$$\cos \theta = \frac{r_1^2 + r_2^2 - r_{12}^2}{2 r_1 r_2}$$

then

$$H_0 = -\frac{1}{2} \left(\frac{\partial^2}{\partial \rho^2} + \frac{5}{\rho} \frac{\partial}{\partial \rho} + \frac{4}{\rho^2} \Box^* \right) - \frac{\mu_0}{\rho} \tag{34}$$

where

$$\Box^* = \frac{1}{\sin^2 \alpha} \left(\frac{\partial}{\partial \alpha} \sin^2 \alpha \frac{\partial}{\partial \alpha} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) \tag{35}$$

and

$$\mu_0 = \sec \frac{\alpha}{2} + \csc \frac{\alpha}{2} .$$

The properties of the operator $\Box^*$ are given in Appendix G.

Let

$$\frac{1}{r_{12}} = \frac{\nu_0}{\rho} \tag{36}$$

where

$$\nu_0 = (1 - \sin\alpha \cos\theta)^{-1/2}.$$

Equation (31) can then be written in the form

$$\left(\frac{\partial^2}{\partial\rho^2} + \frac{5}{\rho}\frac{\partial}{\partial\rho} + \frac{4}{\rho^2}\Box^* + \frac{2\mu_0}{\rho} + 2\epsilon_0 \right)\psi_1 = \tag{37}$$

$$2\left(\frac{\nu_0}{\rho} - \epsilon_1 \right)\psi_0.$$

Expand ψ_0 as power series in the variable ρ

$$\psi_0 = \pi^{-1}\exp\{-\rho(\sin\tfrac{\alpha}{2} + \cos\tfrac{\alpha}{2})\} \tag{38}$$

$$= \sum_{n=0}^{\infty} g_n^{(0)}\rho^n \tag{39}$$

with

$$g_n^{(0)} = \pi^{-1}(-1)^n \frac{(\sin\tfrac{\alpha}{2} + \cos\tfrac{\alpha}{2})^n}{n!}. \tag{40}$$

Assume a similar expansion of ψ_1

$$\psi_1 = \sum_{n=0}^{\infty} g_n^{(1)} \rho^n , \qquad (41)$$

substitute equations (41) and (39) into equation (37) and equate powers of ρ on both sides of this equation. This leads to the following equations for the $g_m^{(1)}$

$$\left(\square^* + \frac{n(n+4)}{4}\right) g_n^{(1)} = \frac{1}{2} \nu_0 g_{n-1}^{(0)} - \frac{1}{2} \epsilon_1 g_{n-2}^{(0)}$$

$$- \frac{1}{2} \mu_0 g_{n-1}^{(1)} - \frac{1}{2} \epsilon_0 g_{n-2}^{(1)} ,$$

$$n = 0, 1, 2, \cdots \qquad (42)$$

where negative subscripts are to be ignored. Note that the boundary condition on ψ_1 required by the fact that the ground state is a para-state is simply

$$\psi_1(\rho, \alpha, \theta) = \psi_1(\rho, \pi - \alpha, \theta) .$$

The first of this set of equations

$$\square^* g_0^{(1)} = 0 \qquad (43)$$

has as its only square-integrable solution

$$g_0^{(1)} = C_0 . \qquad (44)$$

Choose $C_0 = \pi^{-1}$ for convenience.

The next equation

$$\left(\square^* + \frac{5}{4}\right) g_1^{(1)} = \frac{1}{2} \nu_0 \, g_0^{(0)} - \frac{1}{2} \mu_0 \, g_0^{(1)} \qquad (45)$$

has a unique solution by virtue of the fact that the homogeneous equation has no solution, other than the trivial one, obeying the boundary conditions. The solution of equation (45) is

$$g_1^{(1)} = \pi^{-1}\left(\frac{1}{2}\sqrt{1 - \sin\alpha\cos\theta} - \sin\frac{\alpha}{2} - \cos\frac{\alpha}{2}\right). \qquad (46)$$

The third equation is

$$\left(\square^* + 3\right) g_2^{(1)} = \frac{1}{2} \nu_0 \, g_1^{(0)} - \frac{1}{2} \epsilon_1 \, g_0^{(0)} \qquad (47)$$

$$- \frac{1}{2} \mu_0 \, g_1^{(1)} - \frac{1}{2} \epsilon_0 \, g_0^{(1)} .$$

The homogeneous equation corresponding to this case does have square-integrable solutions, unlike equation (45). Thus in order for a unique solution of equation (47) to exist, the inhomogeneous part of that equation (the right hand side) must be orthogonal to the solutions of the homogeneous equation. The general solution of the homogeneous equation is (see Appendix G)

$$g_2^{(H)} = C_{11} Z_{11}(\alpha, \theta) + C_{10} Z_{1,0}(\alpha, \theta) \tag{48}$$

where

$$Z_{1,0}(\alpha, \theta) = \left(\frac{12}{\pi}\right)^{1/2} \cos \alpha \, ,$$

$$\tag{49}$$

$$Z_{1,1}(\alpha, \theta) = \left(\frac{4}{\pi}\right)^{1/2} \sin \alpha \cos \theta .$$

By virtue of the fact that

$$Z_{1,0}(\pi - \alpha, \theta) = - Z_{1,0}(\alpha, \theta)$$

the right hand side of equation (47) is indeed orthogonal to $Z_{1,0}$ but it is found that the right hand side is not orthogonal to $Z_{1,1}$. Therefore no solution to equation (47) exists which obeys the proper boundary conditions. Presumably some formal solution $\tilde{g}_2^{(1)}$ could be found which yields the right side upon substitution into the left side of equation (47), but any such solution would violate the condition

$$\langle Z_{1,1}, (\square^* + 3) \hat{g}_2 \rangle = \langle (\square^* + 3) Z_{1,1}, \hat{g}_2 \rangle = 0 \tag{50}$$

This is essentially what Bartlett realized in 1937[62] although

his coordinates were defined somewhat differently. Fock took the next step. He showed what form an acceptable expansion had. Fock assumed the form of the solution was

$$\psi_1 = \sum_{n=0}^{\infty} \sum_{k=0}^{[\frac{m}{2}]} g_{m,k}^{(1)}(\alpha,\theta) \, \rho^m \left(\log \rho^2\right)^k \tag{51}$$

where the notation $\left[\frac{m}{2}\right]$ means the "integral part of $\frac{m}{2}$".
Substitution of this form into equation (37) yields the following
set of equations for the $g_{m,k}^{(1)}$

$$\left(\square^* + \frac{m(m+4)}{4}\right) g_{n,k}^{(1)} = \frac{1}{2}\left(N_0 \, g_{m-1}^{(0)} - \epsilon_1 \, g_{n-2}^{(0)}\right) \delta_{k,0}$$

$$- (k+1)(m+2) \, g_{m,k+1}^{(1)} - (k+1)(k+2) \, g_{m,k+2}^{(1)}$$

$$- \frac{1}{2} \mu_0 \, g_{m-1,k}^{(1)} - \frac{1}{2} \epsilon_0 \, g_{m-2,k}^{(1)} \, ,$$

$$m = 0,1,2,\cdots \, ,$$
$$k = 0,1,\cdots, \left[\frac{m}{2}\right] \tag{52}$$

where negative subscripts and subscripts on $g_{m,\ell}^{(1)}$ for $\ell \nmid \left[\frac{m}{2}\right]$ are
to be ignored. The equations for $g_{0,0}^{(1)}$ and $g_{1,0}^{(1)}$ are similar to
equations (43) and (45) and have the unique solutions

$$g_{0,0}^{(1)} = \pi^{-1}, \tag{53}$$

$$g_{1,0}^{(1)} = \pi^{-1}\left[\frac{1}{2}\sqrt{1 - \sin\alpha\cos\theta} - \sin\frac{\alpha}{2} - \cos\frac{\alpha}{2}\right]. \tag{54}$$

For n = 2 there are now two equations of the form

$$(\Box^* + 3)\, g_{2,1}^{(1)} = 0 \tag{55}$$

and

$$(\Box^* + 3)\, g_{2,0}^{(1)} = \frac{1}{2}\, \nu_0\, g_1^{(0)} - \frac{1}{2}\, \epsilon_1\, g_0^{(0)}$$
$$- \frac{1}{2}\, \mu_0\, g_{1,0}^{(1)} - \frac{1}{2}\, \epsilon_0\, g_{0,0}^{(1)} - 4\, g_{2,1}^{(1)} \,. \tag{56}$$

The first of these equations is an equation for hyperspherical harmonics. For the ground state the acceptable solution is

$$g_{2,1}^{(1)} = C_{11}\, \sin \alpha \, \cos \theta \,. \tag{57}$$

The constant appearing here is not arbitrary but must be determined by requiring orthogonality of the right side of equation (56) to the solutions of the corresponding homogeneous equation. This gives the constant the value[35,69]

$$C_{11} = \frac{2 - \pi}{6\pi^2} \,. \tag{58}$$

Equation (56) does have a solution of the required type since the orthogonality conditions are now satisfied. For all higher n $(n > 2)$ the same circumstance is met with. If the equations for a given n are solved starting with the largest k possible, all

orthogonality conditions are able to be satisfied and the solutions

do indeed exist. The difficulties encountered are of a computational

nature only but these difficulties have not been overcome and explicit

solutions to the higher order equations have never been given. The

part of the solution which has been explicitly determined is

$$\psi_1 = \pi^{-1}\left(1 - \rho\left[\sqrt{1-\sin\alpha\cos\theta} - \sin\frac{\alpha}{2} - \cos\frac{\alpha}{2}\right]\right.$$

$$+ \frac{2-\pi}{6\pi}\sin\alpha\cos\theta\,\rho^2\log\rho^2 \qquad (59)$$

$$\left. - \frac{2-\pi}{12\pi}\sin\alpha\cos\theta\left[\sin\frac{\alpha}{2}+\cos\frac{\alpha}{2}\right]\rho^3\log\rho^2+\cdots\right)$$

or in terms of the Hylleraas variables s,t,u

$$\psi_1 = \pi^{-1}\left(1 - \frac{1}{2}u + s + \frac{2-\pi}{12\pi}(s^2+t^2-2u^2)\log\left(\frac{s^2+t^2}{2}\right)\right.$$

$$(60)$$

$$\left. - \frac{2-\pi}{24\pi}s(s^2+t^2-2u^2)\log\left(\frac{s^2+t^2}{2}\right)+\cdots\right).$$

In going this far with the solution Fock was able to prove,

subject to the condition that this form for ψ_1 would converge to

a square-integrable result upon summation of the infinite series,

that the form of the solution must contain logarithmic type terms.

There would seem to be very little doubt about the form of the

solution but it should be kept in mind that without any knowledge

of the convergence of this series no definite statement can be made

without further investigation. Fock's original argument was made

for the complete two-electron Schrödinger equation not the first-

order equation, but the argument proceeds in exactly the same way

in either case. It was this work which prompted Hylleraas and

Midtdal[34,70] in 1956, Ermolaev and Sochilin[35] in 1964, and finally

Frankowski and Pekeris[3] in 1966 to study the effect of the inclusion

of logarithmic terms in trial variational wave functions. Although

Hylleraas and Midtdal's results did not clearly favor their

inclusion, Ermolaev and Sochilin's work did indicate that better

wavefunctions could be obtained with fewer terms by including these

logarithmic terms. Finally Frankowski and Pekeris demonstrated

that the form for the wavefunction suggested by Fock led to rapid

convergence when used in the variational principle and were able

to give the most accurate eigenvalue to date for the helium ground

state using 246 terms. This work certainly supports the validity

of Fock's expansion.

Asymptotic Form of Ψ

Another topic which has been the subject of some investigation

is the asymptotic form of the wavefunction for the two-electron

atom. Somehow most chemists, and a few physicists, believe that

the asymptotic form of the wavefunction must be[37], in Z-reduced units

$$\Psi \sim exp\left(-\sqrt{-2E}\,(r_1 + r_2)\right) \tag{61}$$

for r_1 and r_2 large. The literature contains repeated references to wavefunctions "constrained to behave correctly at infinity" when they have the above form. Some workers[71] have wondered why scale-parameters don't converge to the value of $\sqrt{-2E}$ as the size of the basis set is increased. The explanation is simple. Equation (61) does not give the correct asymptotic form of the wavefunction. Fock,[66] in the same paper in which he introduced the logarithmic terms into the wavefunction, discusses the asymptotic form of the wavefunction for large $\rho = \sqrt{r_1^2 + r_2^2}$. His discussion concentrates on the differential equation and in a simple way he shows that a possible asymptotic form is, in Z-reduced units

$$\Psi \sim \exp(-r_1)\exp(-\sqrt{-2E-1}\,r_2) + \exp(-r_2)\exp(-\sqrt{-2E-1}\,r_1). \tag{62}$$

However, Fock's derivation is not rigorous because he simply assumed a form like the above and used the Schrödinger equation to get the "fine points" of the form. Fock did not actually show that the terms in equation (62) actually dominate the exact wavefunction for large r_1 or r_2.

Slaggie and Wichmann[72] have given a rigorous derivation of asymptotic boinds on the wavefunction for a general bound non-relativistic three-body system. These authors were able to show that the wavefunction is dominated by a function of the form, in Z-reduced units

$$F = \frac{\exp\left(-\sqrt{-2E-1}\ r_1\right) + \exp\left(\frac{-\sqrt{-2E}\ r_1^2}{\sqrt{r_1^2 + r_2^2}}\right)}{\exp(r_2) + \exp\left(\frac{\sqrt{-2E}\ r_2^2}{\sqrt{r_1^2 + r_2^2}}\right)}$$

$$+ \frac{\exp\left(-\sqrt{-2E-1}\ r_2\right) + \exp\left(\frac{-\sqrt{-2E}\ r_2^2}{\sqrt{r_1^2 + r_2^2}}\right)}{\exp(r_1) + \exp\left(\frac{\sqrt{-2E}\ r_1^2}{\sqrt{r_1^2 + r_2^2}}\right)} \tag{63}$$

They were not complete, however, in that they did not show that there does not exist a "better" estimate than that given by equation (63). Indeed, this seems very difficult to prove due to the complexity of the analysis. The question of the best asymptotic form is thus still open.

Asymptotic Large-Z Expansion

A different type of direct approach to the solution of the Schrödinger equation has recently been proposed by Mendelsohn[73]. The technique, which is called the "asymptotic large-Z expansion", begins with the assumption that, in ordinary atomic units, the solution may be written as

$$\Psi = \exp\left(-Z\,h(r_1, r_2)\right) \sum_{n=0}^{\infty} \frac{a_n(\vec{r}_1, \vec{r}_2)}{Z^n} \tag{64}$$

where h and the a_n are to be determined. The assumption is also made that

$$E = Z^2 \sum_{n=0}^{\infty} \frac{\epsilon_n}{Z^n} \qquad (65)$$

where the ϵ_n are considered as known. Note that this method does not determine the energy. The forms above for Ψ and E are substituted into the Schrödinger equation

$$\left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right] \Psi = E \Psi \qquad (66)$$

and the coefficients of the various powers of Z are set equal to zero. This leads to the following equations for h and the a_n

$$a_0 \left[(\nabla_1 h)^2 + (\nabla_2 h)^2 + 2\epsilon_0 \right] = 0 , \qquad (67)$$

$$\left[\nabla_1 h \cdot \nabla_1 + \nabla_2 h \cdot \nabla_2 + \frac{1}{2}\left[(\nabla_1^2 + \nabla_2^2) h\right] \right.$$

$$\left. - \frac{1}{r_1} - \frac{1}{r_2} - \epsilon_1 \right] a_0 \qquad (68)$$

$$- \frac{a_1}{2} \left[(\nabla_1 h)^2 + (\nabla_2 h)^2 + 2\epsilon_0 \right] = 0 ,$$

$$[\nabla_1 h \cdot \nabla_1 + \nabla_2 h \cdot \nabla_2 + [\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) h]$$

$$-\frac{1}{r_1} - \frac{1}{r_2} - \epsilon_1] a_{n-1} \tag{69}$$

$$- \frac{a_m}{2}[(\nabla_1 h)^2 + (\nabla_2 h)^2 + 2\epsilon_0]$$

$$- \tfrac{1}{2}[\nabla_1^2 + \nabla_2^2 - \frac{2}{r_{12}}] - \sum_{k=2}^{n} \epsilon_k a_{n-k} = 0,$$

$$n = 2, 3, 4, \cdots$$

Since $\epsilon_0 = -1$ and since h is assumed to be only a function of r_1 and r_2, equation (67) reduces to

$$\left(\frac{\partial h}{\partial r_1}\right)^2 + \left(\frac{\partial h}{\partial r_2}\right)^2 = 2 \tag{70}$$

which has the solution

$$h = r_1 + r_2. \tag{71}$$

In equation (71) the coefficient of a_1 vanishes. Using the relationships

$$\nabla_1 = \hat{r}_1 \frac{\partial}{\partial r_1} + \hat{r}_{12} \frac{\partial}{\partial r_{12}}, \tag{72a}$$

$$\nabla_2 = \hat{r}_2 \frac{\partial}{\partial r_2} - \hat{r}_{12} \frac{\partial}{\partial r_{12}} , \tag{72b}$$

$$\hat{r}_1 \cdot \hat{r}_{12} = \frac{r_1^2 - r_2^2 + r_{12}^2}{2 r_1 r_{12}} , \tag{73a}$$

$$-\hat{r}_2 \cdot \hat{r}_{12} = \frac{r_2^2 - r_1^2 + r_{12}^2}{2 r_2 r_{12}} , \tag{73b}$$

and the form above for h in equation (68) gives the following equation for a_o

$$\left[\frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} + \frac{1}{2 r_{12}} \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{r_1} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2} \right) \frac{\partial}{\partial r_{12}} \right.$$
$$\left. - \epsilon_1 \right] a_o = 0 . \tag{74}$$

A particular solution of this equation is

$$a_o = exp\left(\frac{\epsilon_1}{2} (r_1 + r_2) \right) . \tag{75}$$

Equation (69) for $n = 2$ similarly becomes

$$\left[\frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} + \frac{1}{2 r_{12}} \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{r_1} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2} \right) \frac{\partial}{\partial r_{12}} \right.$$
$$\left. - \epsilon_1 \right] a_1 = \frac{1}{2} \left[\nabla_1^2 + \nabla_2^2 - \frac{2}{r_{12}} + 2 \epsilon_2 \right] a_o \tag{76}$$

which is an equation for a_1 . Let

$$a_1 = f_1 a_0 \qquad (77)$$

where a_0 is given by equation (75). The equation for f_1 is

$$\left[\frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} + \frac{1}{2 r_{12}} \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{r_1} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2} \right) \frac{\partial}{\partial r_{12}} \right] f_1$$

$$\qquad (78)$$

$$= \frac{\epsilon_1^2}{4} + \epsilon_2 + \frac{\epsilon_1}{2} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) - \frac{1}{r_{12}} \;.$$

If the independent variables are chosen as $s = r_1 + r_2$, $t = r_1 - r_2$, and $\cos \theta$ where θ is the angle between $\vec{r_1}$ and $\vec{r_2}$ (instead of r_1 , r_2 , and r_{12}) this equation becomes

$$\frac{\partial f_1}{\partial s} = \frac{\epsilon_1^2}{8} + \frac{\epsilon_2}{2} + \frac{\epsilon_1 s}{s^2 - t^2} - \left(2 \left[s^2 (1 - \cos \theta) + t^2 (1 + \cos \theta) \right] \right)^{-\frac{1}{2}}$$

$$\qquad (79)$$

The author of this thesis is not sure of the boundary conditions which Mendelsohn uses to completely determine the solution of this equation but Mendelsohn gives the result as

$$f_1 = \frac{1}{2} \left[\frac{\epsilon_1^2}{4} + \epsilon_2 \right] s + \frac{\epsilon_1}{2} \log \left(\frac{s^2 - t^2}{4} \right) \qquad (80)$$

$$- \frac{1}{2 \sin \frac{\theta}{2}} \log \left[\frac{\left(\frac{s^2 [1 - \cos \theta] + t^2 [1 + \cos \theta]}{2} \right)^{1/2} + (\sin \frac{\theta}{2}) s}{(1 + \sin \frac{\theta}{2}) |t|} \right] .$$

Thus the solution to order Z^{-1} given by Mendelsohn is

$$\Psi = exp\left(-[Z - \frac{\epsilon_1}{2}][r_1 + r_2]\right)\left[1 + \frac{1}{Z}\left(\frac{\epsilon_1}{2}\log r_1 r_2\right.\right.$$

$$+ \frac{1}{2}\left(\frac{\epsilon_1^2}{4} + \epsilon_2\right)(r_1 + r_2) - \frac{1}{2\sin\frac{\theta}{2}}\log\left[\frac{r_{12} + \sin\frac{\theta}{2}(r_1 + r_2)}{(1 + \sin\frac{\theta}{2})|r_1 - r_2|}\right]$$

$$+ \cdots \Big]$$

$$(81)$$

This solution diverges logarithmically at $r_1 = r_2$, and if $\theta = 0$

the divergence becomes a first-order pole. Mendelsohn argues that

this solution is not valid near the singularities of the potential

and that special techniques ("stretching and matching") must be

applied in these regions. In doing this Mendelsohn arrives at

forms of the wavefunction which are valid near certain singularities

in the potential, but these solutions are found to contain terms

like $\frac{\log Z}{Z}$. Since Kato[51] has shown that, in Z-reduced atomic

units, a perturbation series in powers of Z^{-1} converges to the

true wavefunction, and since even if the units are changed to

Z-reduced units Mendelsohn's solution is not of this form the author

feels that more experience is necessary in using the above type

of expansion (asymptotic large-Z) in order to decide what is going

wrong, if anything.

Numerical Techniques

Numerical techniques have also been used to obtain approximate solutions of the Schrödinger equation for helium. Bartlett[74,75] replaced the differential equation by a difference equation and used a numerical iteration procedure to solve this difference equation. However he couldn't determine the energy to better than -2.90 ± 0.01 using this technique even though the fluctuations in a quantity called the local energy

$$E_{loc}(\vec{r}_1, \vec{r}_2) = \frac{H\psi}{\psi} \qquad (82)$$

for his wavefunction were small, between -2.88 and -2.92, for all values of r_1 and r_2 up to $4B$. Frost[76,77,78] used the constancy of this local energy as a criterion to determine an approximate wave function. This technique, called the local-energy method, consists in evaluating the local energy by equation (82) at a certain number of coordinate points using a trial wave function with arbitrary parameters and then determining these parameters by requiring the variance in the energy to be minimized. Since no integrals need be carried out this method could have some practical advantage over the variation method if good results can be obtained for larger systems than helium. The ground state energy of helium has been calculated by this method as -2.9025, compared with the more accurate value of -2.9037.

Kalos[79] has given a Monte Carlo technique for generating a density function proportional to Ψ^2 for helium by use of the Green's function for the diffusion operator containing the repulsive interaction. He used an iterative technique to get approximate values of $\langle r_i^2 \rangle$ as a test of the goodness of Ψ^2 and obtained

$$\langle r_i^2 \rangle = 1.193$$

compared to Pekeris's value[37,38] of

$$\langle r_i^2 \rangle = 1.19348.$$

The agreement is good but the expenditure is also great. To produce the results quoted above, Kalos carried out eighty-one iterations and each iteration took three-five minutes on a CDC 6600 computer.

Other Attempts

Attempts have also been made to study the two-electron Schrödinger equation by means of the Green's function technique, but most of these efforts begin with the free particle Green's function[80] and are thus cumbersome and difficult to iterate analytically a sufficient number of times to be interesting. Jasperse and Friedman[81] have made some headway by transforming the integral equations to momentum space and then expanding the wave function in terms of a convenient complete set. They then

truncate the expansion and obtain a numerical solution to the coupled integral equations. With a fourth order truncation Jasperse and Friedman are able to obtain the value -2.9001 for the ground state energy (compared to -2.9037). They are also able to obtain estimates on some excited state energies. One drawback of the technique is its present lack of a variational basis so that bounds on the energy (and associated error estimates) are difficult to obtain.

A direct study of the Schrödinger equation in momentum space has been made by McWeeny and Coulson.[82] They considered the possibility of solving the integral equation which arises by an iterative technique but concluded that more than one iteration would be an extremely formidable task. Thus no really accurate wavefunction is available in momentum space, since the Hylleraas type wavefunction proves impossible to transform directly.

III. AN EXACT SOLUTION TO THE SCHRÖDINGER EQUATION FOR THE TWO-ELECTRON ATOM

The solution of the Schrödinger equation for the problem of two or more electrons interacting with each other and with a number of fixed nuclei contains the theoretical explanation of much of physics and most of chemistry. An explicit solution of this equation for all but the simplest cases certainly seems to be out of the range of our present mathematical abilities, but the author feels that the solution of the Schrödinger equation for two-electron systems is now within reach. The reason for this optimistic statement is the recent discovery of a convenient set of recursion relations which considerably reduce the labor associated with a partial series expansion of the exact solution, and which permit the direct realization of the explicit form of the exact solution.

Many of the ideas used in the attack presented here on the actual two-electron atom can be better appreciated after a study of two model atomic systems. A treatment of these model systems, the Hooke's law atom and the one dimension delta function atom, reveals that certain features of the solution for the actual two-electron atom are mirrored in the more easily obtainable solutions to the model systems and clearly demonstrates the usefulness of models when dealing with a difficult situation.

1. The Hooke's Law Model for the Two-Electron Atom

In the actual two-electron atom the electrons interact with each other and with a fixed center, the nucleus, by means of Coulombic forces. In the Hooke's law model for the two-electron atom the electrons still interact with each other by a Coulombic force, but they interact with the nucleus by means of a Hooke's law force.

The Schrödinger equation for this model atomic system is

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{e^2}{r_{12}} - \mathcal{E} \right]\Psi = 0 \qquad (1)$$

where m is the reduced mass of the electron, k is the force constant of the electron-nucleus oscillator and r_1, r_2 and r_{12} represent the usual metric variables in the two-electron problem. If k is chosen to be z^4 for convenience and if Z-reduced atomic units are used, equation (1) may be written as

$$\left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}(r_1^2 + r_2^2) + \frac{1}{Z r_{12}} - E \right]\Psi = 0 \qquad (2)$$

which is analogous in form to the Z-reduced helium equation. Appended to this thesis is a discussion of the solution of this equation for the ground state, and the results obtained there will simply be quoted, not derived, here.

Due to the separability of equation (2) in the center of mass and relative coordinates a perturbation solution exact to first order

in $\lambda = Z^{-1}$ is able to be given. In terms of the variables r_1, r_2, and r_{12} this solution is

$$\Psi(r_1, r_2, r_{12}) = \psi_0 + \frac{1}{Z} \psi_1 + O\left(\frac{1}{Z^2}\right) \tag{3}$$

where

$$\psi_0 = \pi^{-3/2} \exp\left[-\frac{1}{2}(r_1^2 + r_2^2)\right], \tag{4}$$

and

$$\psi_1 = \psi_0 \left[\frac{1}{r_{12}} - \frac{\exp\left(\frac{1}{2} r_{12}^2\right) \operatorname{erfc}\left(\frac{r_{12}}{\sqrt{2}}\right)}{r_{12}} \right.$$
$$\left. + 2^{1/2} \int_0^{r_{12}/\sqrt{2}} e^{s^2} \operatorname{erfc} s \, ds - \left(\frac{2}{\pi}\right)^{1/2}(1 + \log 2) \right], \tag{5}$$

where

$$\operatorname{erfc} x = \frac{2}{\pi^{1/2}} \int_x^\infty e^{-t^2} dt .$$

ψ_1 may expanded in a power series in the variable r_{12}. The result is

$$\psi_1 = \psi_0 \left[-\left(\frac{2}{\pi}\right)^{1/2} \log 2 + \sum_{n=1}^{\infty} \frac{(-1)^{n+1} r_{12}^{n}}{n\left(\frac{n+1}{2}\right)! \, 2^{\frac{n+1}{2}}} \right]$$

$$= \psi_0 \left[-\left(\frac{2}{\pi}\right)^{1/2} \log 2 + \frac{1}{2} r_{12} - \frac{1}{3(2\pi)^{1/2}} r_{12}^2 \right.$$

$$\left. + \frac{1}{24} r_{12}^3 - \frac{1}{30(2\pi)^{1/2}} r_{12}^4 + \cdots \right] \qquad (6)$$

The energy may thus be determined exactly through third order in

$$\lambda = Z^{-1}$$

$$E = \epsilon_0 + Z^{-1} \epsilon_1 + Z^{-2} \epsilon_2 + Z^{-3} \epsilon_3 + O(Z^{-4}) \qquad (7)$$

with

$$\epsilon_0 = 3, \qquad (8a)$$

$$\epsilon_1 = \left(\frac{2}{\pi}\right)^{1/2} = 0.797884\ldots, \qquad (8b)$$

$$\epsilon_2 = -\left(\frac{2}{\pi}\right)\left(1 + \log 2 - \frac{\pi}{2}\right) = -0.0778909\cdots, \qquad (8c)$$

and

$$\epsilon_3 = \left(\frac{2}{\pi}\right)^{3/2}\left(2(1-\ell) - \frac{3\pi}{2} + (\pi+3)\log 2\right.$$

$$\left. + \frac{3}{2}\log^2 2 - \frac{\pi^2}{24}\right) = 0.0112528\cdots \qquad (8d)$$

where ℓ is Catalan's constant (ℓ = 0.915965 ...).
Higher order energy coefficients have been determined numerically[83] and
are presented in Table 7.

A study will now be made of equation (2) without carrying out
the separation of variables. The object will be to study how much
progress can be made in solving the first-order perturbation equation
for the Hooke's law atom without explicit separation of variables
in the hopes of obtaining a technique which is applicable to the
similar first-order perturbation equation for the helium atom.

The first order equation for the Hooke's law atom is (compare
equation (II.15)) is

$$\left(H_0 - \epsilon_0\right)\psi_1 = \left(\epsilon_1 - \frac{1}{r_{12}}\right)\psi_0 \qquad (9)$$

where

$$H_o = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{2}\left(r_1^2 + r_2^2\right),$$

$$\psi_o = \pi^{-3/2} \exp\left[-\frac{1}{2}\left(r_1^2 + r_2^2\right)\right],$$

$$\epsilon_o = 3,$$

and

$$\epsilon_1 = \left(\frac{2}{\pi}\right)^{1/2}.$$

If the three independent variables for the ground state are taken as the metric variables r_1, r_2, r_{12} then (see Appendix B)

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2 + \frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2}r_{12}$$

$$+ \frac{4\vartheta}{r_{12}}\frac{\partial}{\partial r_{12}} + 4\vartheta' r_{12}\frac{\partial}{\partial r_{12}}, \tag{10}$$

where

$$\vartheta = \frac{1}{4}\left(r_1^2 - r_2^2\right)\left(\frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right) \tag{11a}$$

$$\mathcal{D}' = \frac{1}{4}\left(\frac{1}{r_1}\frac{\partial}{\partial r_1} + \frac{1}{r_2}\frac{\partial}{\partial r_2}\right). \qquad (11b)$$

Assume that the particular solution sought for ψ_1 may be expanded as a power series in r_{12} beginning with the power σ

$$\psi_1 = \sum_{n=0}^{\infty} r_{12}^{n+\sigma}\, \varphi_n(r_1, r_2) \qquad (12)$$

with coefficients which are functions of r_1 and r_2 to be determined. Substitution of this form for ψ_1 into equation (9) results in the equation

$$-\sigma\, r_{12}^{\sigma-2}\left(2\mathcal{D} + \sigma + 1\right)\varphi_0$$

$$-(\sigma+1)\, r_{12}^{\sigma-1}\left(2\mathcal{D} + \sigma + 2\right)\varphi_1$$

$$-\sum_{n=2}^{\infty} r_{12}^{n+\sigma-2}\Big((n+\sigma)(2\mathcal{D}+n+\sigma+1)\varphi_n$$

$$- (H_0' - \epsilon_0 - 2(n+\sigma-2)\mathcal{D}')\,\varphi_{n-2}\Big)$$

$$= -r_{12}^{-1}\psi_0 + \epsilon_1\psi_0, \qquad (13)$$

where

$$H_0' = -\frac{1}{2}\left(\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}r_2\right) + \frac{1}{2}\left(r_1^2 + r_2^2\right).$$

Since it is known that the first order wavefunction may contain some amount of the zeroth order wavefunction, the contribution being fixed by the orthogonality condition

$$\langle \psi_1, \psi_0 \rangle = 0 \tag{14}$$

the value of σ cannot be greater than zero. It may be argued that the first order wavefunction need not contain any amount of the zeroth order wavefunction and though this is true, it is equally true that in general it may and this must be accounted for by the form assumed for ψ_1. Suppose σ is less than zero, say

$$\sigma = -N \quad , N > 0. \tag{15}$$

The equation for ϕ_0 is then

$$(2\mathcal{D} - N + 1)\phi_0 = 0 \tag{16}$$

and

$$\phi_0 = \frac{f\left(r_1^2 + r_2^2\right)}{\left(r_1^2 - r_2^2\right)^{\frac{1-N}{2}}} \tag{17}$$

where f is not determined. This means that

$$\psi_1 = \frac{(r_1^2 - r_2^2)^{\frac{N-1}{2}}}{r_{12}^N} \; f(r_1^2 + r_2^2) + \cdots \qquad (18)$$

and as $r_{12} \to 0$, ψ_1 diverges. But Kato's work[5,64,65] requires that ψ_1 remain bounded. Therefore σ must be zero. With $\sigma = 0$, the equations for the φ_m, assuming independence of the powers of r_{12}, are

$$(\mathcal{D} + 1)\, \varphi_1 = \frac{1}{2}\, \psi_0 , \qquad (19)$$

$$\left(\mathcal{D} + \frac{3}{2}\right) \varphi_2 - \frac{1}{4}\left(H_0' - \epsilon_0\right) \varphi_0 = -\frac{1}{4}\, \epsilon_1\, \psi_0 , \qquad (20)$$

$$\left(\mathcal{D} + \frac{n+1}{2}\right) \varphi_n = \frac{1}{2n}\left(H_0' - \epsilon_0 - 2(n-2)\mathcal{D}'\right) \varphi_{n-2},$$

$$n > 2 . \qquad (21)$$

The coefficients of the odd powers of r_{12} can be determined by the recursive integration of these equations, beginning with equation (19). The determination of the coefficient of the even powers of r_{12} presents a new difficulty. There is no equation to determine φ_0, and so φ_0 must be determined by some other means. In fact the only requirements on ψ_1 not explicit in equations (19), (20) and (21) are the boundary conditions associated with this problem. These conditions are

$$\langle \psi_1, \psi_1 \rangle < \infty , \tag{22}$$

$$\langle (\nabla_1^2 + \nabla_2^2) \psi_1, (\nabla_1^2 + \nabla_2^2) \psi_1 \rangle < \infty , \tag{23}$$

$$\langle \Phi, (\nabla_1^2 + \nabla_2^2) \psi_1 \rangle = \langle (\nabla_1^2 + \nabla_2^2) \Phi, \psi_1 \rangle , \tag{24}$$

where Φ is any function contained in the domain $\mathcal{D}_0$ of the Hamiltonian H . To proceed with the determination of φ_0 write φ_0 in the form

$$\varphi_0 = C_0 \psi_0 + \varphi_0' \tag{25}$$

where φ_0' is to be chosen to make ψ_1 satisfy the boundary conditions above. If the variables are taken as

$$x = r_1^2 + r_2^2 , \qquad y = r_1^2 - r_2^2 \tag{26}$$

with ranges $(0, \infty)$ and $(-x, +x)$, then

$$\mathcal{D} = y \frac{\partial}{\partial y} , \qquad \mathcal{D}' = \frac{\partial}{\partial x} , \tag{27}$$

$$H_0' = -2\left[x\frac{\partial^2}{\partial x^2} + 3\frac{\partial}{\partial x} + 2y\frac{\partial^2}{\partial x \partial y} + x\frac{\partial^2}{\partial y^2} \right]$$
$$+ \frac{1}{2}x \quad , \tag{28}$$

and

$$\psi_0 = \pi^{-3/2} \exp\left(-\frac{1}{2}x\right) . \tag{29}$$

Equations (19) - (21) become

$$\frac{\partial}{\partial y}\left(y\,\varphi_1\right) = \frac{1}{2}\psi_0 , \tag{30}$$

$$\frac{\partial}{\partial y}\left(y^{3/2}\varphi_2\right) = -\frac{1}{4}\epsilon_1 y^{1/2}\psi_0 + \frac{1}{4}y^{1/2}(H_0'-\epsilon_0)\varphi_0 , \tag{31}$$

$$\frac{\partial}{\partial y}\left(y^{\frac{n+1}{2}}\varphi_n\right) = y^{\frac{n-1}{2}}\left(\frac{1}{2n}(H_0'-\epsilon_0) + \left(\frac{2}{n}-1\right)\mathcal{D}'\right)\varphi_{n-2} ,$$
$$n > 2 . \tag{32}$$

These equations may be integrated explicitly. The square-integrable

solution to equation (30) is

$$y \, \phi_1 = \frac{1}{2} \int_0^y \psi_0(x, z) \, dz \, ,$$

(33)

or

$$\phi_1 = \frac{1}{2} \psi_0$$

(34)

since ψ_0 is independent of y.

Partition each of ϕ_{2k} in the same way as ϕ_0 in equation

(25), that is let a prime indicate a recurrence back to ϕ_0'. Then

$$y^{3/2} \phi_2 = - \frac{\epsilon_1}{4} \int_0^y z^{1/2} \psi_0(x, z) \, dz + \frac{1}{4} \int_0^y z^{1/2} (H_0' - \epsilon_0) \phi_0' \, dz$$

(35)

or

$$\phi_2 = - \frac{\epsilon_1}{6} \psi_0 + \phi_2' \, ,$$

(36)

where

$$\phi_2' = \frac{1}{4} y^{-3/2} \int_0^y z^{1/2} (H_0' - \epsilon_0) \phi_0' (x, z) \, dz.$$

(37)

Continuation in this manner gives

$$\psi_1 = C_0 \psi_0 \ + \ \sum_{n=0}^{\infty} \frac{\psi_0 \, r_{12}^{2n+1}}{(2n+1)(n+1)! \, 2^{n+1}}$$

$$- \sum_{n=1}^{\infty} \frac{\psi_0 \, \epsilon_1 \, r_{12}^{2n}}{2n(2n+1)!!} \ + \ \psi_1' , \tag{38}$$

where

$$\psi_1' = \varphi_0' + \varphi_2' \, r_{12}^2 + \cdots \tag{39}$$

and $(2n + 1)!! = (2n + 1)(2n - 1) \ldots 3.1$.

In this case a summation of the series in equation (38) shows that $\psi_1' = 0$ since the solution already obeys the correct boundary conditions without any contribution from ψ_0. That this is indeed the correct solution may be verified by comparison with equation (8).

In Appendix E it is shown that if the solution ψ_1 is expanded in a Legendre series in $\cos \Theta$ where θ is the angle between the radius vectors $\vec{r}_1$ and $\vec{r}_2$

$$\psi_1 = \psi_0 \sum_{\ell=0}^{\infty} f_\ell(r_1, r_2) \, P_\ell(\cos \Theta) \tag{40}$$

then for large ℓ the f_ℓ behave as follows

$$f_\ell = \frac{f^{(-1)}}{(\ell+\frac{1}{2})^2} + \frac{f^{(-2)}}{(\ell+\frac{1}{2})^4} + \cdots \qquad (41)$$

where

$$f^{(-1)} = -\frac{1}{4} S(1+2\eta) \exp(-2\eta), \qquad (42)$$

$$f^{(-2)} = -\frac{1}{4} S\left[\left(-\frac{4}{3}\eta^4 + \frac{1}{3}\eta^3 + \frac{3}{2}\eta^2 + 2\eta \right.\right.$$

$$\left.\left. +1\right) - S^2\left(\frac{1}{4}\eta^2 + \frac{3}{8}\eta + \frac{3}{16}\right)\right]\exp(-2\eta),$$

$$(43)$$

and

$$S = r_1 + r_2, \qquad (44)$$

$$\eta = \frac{|r_2 - r_1|}{r_1 + r_2}\left(\ell+\frac{1}{2}\right). \qquad (45)$$

It should be possible to derive this form for f_ℓ and the values of $f^{(-n)}$ from the series expansion given in equation (38). Let

$$r_{12}^n = \sum_{\ell=0}^{\infty} R_{n,\ell}(r_1, r_2)\, P_\ell(\cos\theta) , \qquad (46)$$

where the $R_{n,\ell}$ have been given by Sack[84]. The $R_{n,\ell}$ used here are $R_{1,\ell}$ and $R_{3,\ell}$ and these are

$$R_{1,\ell} = \frac{1}{2\ell+3}\, \frac{r_<^{\ell+2}}{r_>^{\ell+1}} - \frac{1}{2\ell-1}\, \frac{r_<^{\ell}}{r_>^{\ell-1}} , \qquad (47)$$

and

$$R_{3,\ell} = \frac{3}{4(\ell-\frac{1}{2})(\ell-\frac{3}{2})}\, \frac{r_<^{\ell}}{r_>^{\ell-3}} - \frac{3}{2(\ell-\frac{1}{2})(\ell+\frac{3}{2})}\, \frac{r_<^{\ell+2}}{r_>^{\ell-1}}$$

$$+ \frac{3}{4(\ell+\frac{3}{2})(\ell+\frac{5}{2})}\, \frac{r_<^{\ell+4}}{r_>^{\ell+1}} . \qquad (48)$$

Substitution of equation (46) into equation (38) and comparison with equation (40) leads to the result

$$f_\ell = \frac{1}{2} R_{1,\ell} + \frac{1}{24} R_{3,\ell} + \cdots \qquad (49)$$

for large ℓ . But

$$R_{1,\ell} = -\frac{1}{2} \frac{S(1+2y)\exp(-2y)}{(\ell+\frac{1}{2})^2}$$

$$-\frac{1}{2} \frac{S(1+2y+\frac{3}{2}y^2+\frac{1}{3}y^3-\frac{4}{3}y^4)\exp(-2y)}{(\ell+\frac{1}{2})^4}$$

$$+ O(\ell^{-6}) \tag{50}$$

and

$$R_{3,\ell} = \frac{3}{8} \frac{S^3(3+6y+4y^2)\exp(-2y)}{(\ell+\frac{1}{2})^4} \tag{51}$$

$$+ O(\ell^{-6}),$$

where S and y are given by equations (44) and (45).

Therefore substitution of equations (50) and (51) into equation (49) yields

$$f_\ell = -\frac{1}{4} \frac{S(1+2y)\exp(-2y)}{(\ell+\frac{1}{2})^2}$$

$$-\frac{1}{4} \frac{S\exp(-2y)}{(\ell+\frac{1}{2})^4}\left[\left(-\frac{4}{3}y^4+\frac{1}{3}y^3+\frac{3}{2}y^2+2y\right.\right.$$

$$\left.\left.+1\right)-S^2\left(\frac{1}{4}y^2+\frac{3}{8}y+\frac{3}{16}\right)\right]$$

$$+ O(\ell^{-6}) \tag{52}$$

in complete agreement with equations (42) and (43), which is, of course, expected.

Thus the solution, through first order, of the problem of two electrons interacting coulombically with each other and harmonically with a fixed center is solvable by assuming a simple power series in the interelectronic distance and by using only simple first-order differential recursion relations to generate the coefficients. Some difficulty arose with the coefficients of the even powers in that the lowest coefficient, independent of r_{12} , was not determined by the recursive equations themselves. For the Hooke's law atom, this difficulty was able to be overcome by a direct summation of the power series. Indeed, it is difficult to see how to determine the lowest coefficient without a direct summation of the series.

2. The One-Dimensional Delta Function Model for the Two-Electron Atom

The Hooke's law model for the two-electron atom is unlike the actual two-electron atom in several ways, but a major difference between the two is that the Schrödinger equation for the former is separable, while that of the latter is essentially non-separable. Therefore, although certain features of the real atom are predicted by the Hooke's law model, others are not even hinted at.

A model atom which has an essentially non-separable Schrödinger equation but which is simpler than the actual two-electron atom is the one-dimensional delta function model. W. Byers Brown[85] has carried out an extensive study of this model and pertinent results from his analysis will simply be quoted, not derived, here.

In Z-scaled atomic units the Schrödinger equation for this model is

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \delta(x) - \delta(y) + \lambda\delta(x-y) \right.$$
$$\left. - E \right] \Psi = 0 \tag{53}$$

where $\lambda = Z^{-1}$

and the variables have the ranges $\infty > x, y > -\infty$.

By integrating this equation over ϵ neighborhoods of the singularities it may be shown that the following conditions must characterize the solution

$$\left(\frac{\partial \Psi}{\partial x}\right)_{0^+} - \left(\frac{\partial \Psi}{\partial x}\right)_{0^-} = -2\Psi(0,y), \text{ all } y \qquad (54a)$$

$$\left(\frac{\partial \Psi}{\partial y}\right)_{0^+} - \left(\frac{\partial \Psi}{\partial y}\right)_{0^-} = -2\Psi(x,0), \text{ all } x \qquad (54b)$$

$$\left(\frac{\partial \Psi}{\partial(x-y)}\right)_{x=y} = \frac{1}{2}\lambda\Psi(x,x), \text{ all } x \qquad (54c)$$

and

$$\left(\frac{\partial \Psi}{\partial(x+y)}\right)_{x=-y} = 0, \text{ all } x, y. \qquad (54d)$$

Of course the standard conditions of square-integrability and continuity also apply to Ψ.

If a perturbation expansion is assumed for Ψ and E (no proof of convergence has been given for this case)

$$\Psi = \sum_{n=0}^{\infty} \lambda^n \psi_n, \qquad (55)$$

and

$$E = \sum_{n=0}^{\infty} \lambda^n \epsilon_n, \qquad (56)$$

then the zeroth order problem

$$\left(H_0 - \epsilon_0\right)\psi_0 = 0 \tag{57}$$

where

$$H_0 = -\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \delta(x) - \delta(y)$$

has as its only bound state solution

$$\psi_0 = exp\left[-|x| - |y|\right] \tag{58}$$

with

$$\epsilon_0 = -1, \tag{59}$$

and

$$\epsilon_1 = \langle \psi_0, \delta(x-y)\psi_0 \rangle$$

$$= \frac{1}{2}. \tag{60}$$

The first order perturbation equation for this model is

$$\left(H_0 - \epsilon_0\right)\psi_1 = \left(\epsilon_1 - \delta(x-y)\right)\psi_0 . \tag{61}$$

The first-order wavefunction may be decomposed into even and odd
parts

$$\psi_1 = \psi_+^{(1)} + \psi_-^{(1)} \tag{62}$$

where

$$\psi_\pm^{(1)}(-x,y) = \pm\,\psi_\pm^{(1)}(x,y) = \psi_\pm^{(1)}(x,-y) \tag{63}$$

and the $\psi_+^{(1)}$ and $\psi_-^{(1)}$ can be determined to be

$$\psi_+^{(1)} = \frac{1}{4}\left(|x+y| + |x-y| - \frac{3}{2}\right)\exp(-|x|-|y|) \tag{64}$$

and

$$\psi_-^{(1)} = \frac{1}{2\pi}\int_r^\infty \left(\sqrt{\frac{r^2-\zeta^2}{s^2-\zeta^2}} - \sqrt{\frac{r^2-\eta^2}{s^2-\eta^2}}\right)K_0(s)\,s\,ds \tag{65}$$

where

$$\zeta = x + y,$$

$$\eta = x - y,$$

$$r^2 = 2(x^2 + y^2),$$

and   Ko   is the modified Bessel function of degree zero

$$K_0(S) = \int_0^\infty \frac{\cos(St)}{\sqrt{1+t^2}}\, dt \,.$$

(66)

An alternative representation of $\psi_-^{(1)}$ is

$$\psi_-^{(1)} = \phi(|\eta|, |\xi|) - \phi(|\xi|, |\eta|),$$

(67)

where

$$\phi(\alpha, \beta) = \frac{1}{2\pi} \int_0^\infty \frac{\cos(k\alpha)\exp(-\beta\sqrt{1+k^2})\, dk}{(1+k^2)^{3/2}} \,.$$

(68)

Using this first order wavefunction the second and third order energies may be computed and are found to be

$$\epsilon_2 = \frac{2}{3\pi} - \frac{3}{8} = -0.16279\ldots$$

(69)

and

$$\epsilon_3 = \frac{1}{6\pi} - \frac{5}{128} = 0.013989\ldots \,.$$

(70)

In order to appreciate the similarity between the delta-function model and the actual two-electron atom rewrite equation 53 in polar coordinates

$$X = \rho \cos \varphi,$$

$$y = \rho \sin \varphi \tag{71}$$

as

$$\left[-\frac{1}{2} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \varphi^2} \right) - \frac{\mu_0}{\rho} + \frac{\lambda \nu_0}{\rho} - E \right] \Psi = 0 \tag{72}$$

where

$$\mu_0(\varphi) = \delta(\varphi) + \delta\left(\varphi - \frac{\pi}{2}\right) + \delta(\varphi - \pi) + \delta\left(\varphi - \frac{3\pi}{2}\right), \tag{73}$$

and

$$\nu_0(\varphi) = \delta\left(\varphi - \frac{\pi}{4}\right) + \delta\left(\varphi - \frac{5\pi}{4}\right). \tag{74}$$

For $\lambda = 0$ the solution to this equation is

$$\psi_0 = e^{-\rho(|\sin \varphi| + |\cos \varphi|)} \tag{75}$$

and may certainly be expanded in a power series in the metric variable ρ. It is logical, then, to assume a power series form for the solution when $\lambda \neq 0$

$$\Psi = \sum_{n=0}^{\infty} \rho^n g_n(\varphi) \tag{76}$$

where the g_n are to be determined.

Substitution of this form for Ψ into equation (72) leads to the following equations for the g_n

$$\frac{d^2}{d\varphi^2} g_0 = 0, \tag{77}$$

$$\left(\frac{d^2}{d\varphi^2} + 1\right) g_1 = 2\lambda \nu_0 g_0 - 2\mu_0 g_0, \tag{78}$$

$$\left(\frac{d^2}{d\varphi^2} + n^2\right) g_n = (2\lambda \nu_0 - 2\mu_0) g_{n-1} \tag{79}$$
$$- 2 E g_{n-2}, \quad n \geq 2.$$

The above are inhomogeneous equations for the g_n and possess solutions only if the inhomogeneous part, or right hand side, of each is orthogonal to the solutions of the corresponding homogeneous equation. The first equation, equation (77), possesses a solution (which must be periodic in φ with period 2π) which may be taken to be

$$g_0 = 1. \tag{80}$$

The solutions to the homogeneous equation corresponding to equation (78) are

$$\sin \varphi, \quad \cos \varphi \tag{81}$$

and the right hand side of equation (78) is orthogonal to both of these functions. A solution of equation (78) thus exists and may be found to be

$$g_1 = 2^{1/2} \lambda \left[\left(H(\varphi - \tfrac{\pi}{4}) - H(\varphi - \tfrac{5\pi}{4}) \right) \sin \varphi \right.$$
$$\left. + \left(H(\tfrac{\pi}{4} - \varphi) - H(\tfrac{5\pi}{4} - \varphi) \right) \cos \varphi \right]$$
$$- 2 \left[\left(H(\varphi) - H(\varphi - \pi) \right) \sin \varphi \right.$$
$$\left. + \left(H(\tfrac{\pi}{2} - \varphi) - H(\tfrac{3\pi}{2} - \varphi) \right) \cos \varphi \right] \tag{82}$$

where $H(x)$ is the Heaviside step function

$$H(x) = \begin{cases} +1 & x > 0 \\ 0 & x < 0 \end{cases} \tag{83}$$

But now it is found that for $n=2$ the right hand side of equation (79) is not orthogonal to the homogeneous solutions

$$\sin 2\varphi, \quad \cos 2\varphi. \tag{84}$$

Therefore equation (79) for n=2 possesses no solution which obeys the proper boundary conditions and the form assumed for Ψ by equation (76), a simple power series in ρ , is incorrect.

This is exactly what happens in the actual two-electron atom as will be seen from a comparison of equation (II.37) - (II.50) with the above.

This result is actually borne out, through first order, by the explicit wave function given by equation (62). Although a treatment for all x,y is difficult, for x=y the form of ψ_1 is

$$\psi_1 = \frac{1}{2}\left[|X| - \frac{3}{4}\right]\exp(-2|X|) - \frac{X}{\pi}K_{\lambda_1}(2X) \qquad (85)$$

where

$$K_{\lambda_1}(X) = \int_0^\infty \frac{\exp[-X\cosh t]}{\cosh t}\,dt \qquad (86)$$

and

$$\cosh t = \frac{1}{2}\left[\exp(t) + \exp(-t)\right]. \qquad (87)$$

For small $|X|$ an expansion of $\psi_1(X,X)$ may be made and is of the form

$$\psi_1(X,X) = -\frac{3}{8} + \frac{3}{4}|X| - \frac{2X^2}{\pi}\log|X|$$
$$+ O(X^2) \qquad (88)$$

which shows explicitly that a power series in ρ is not possible

through first order. Note, however, that higher powers of the logarithm do not occur in this case, at least for $x=y$, whereas the corresponding form for the actual atom contains an infinite number of logarithm terms.

Table 7 contains the perturbation energy coefficients and the correlation energy coefficients ($E_{corr} = E_{ex} - E_{HF}$) for the two models discussed here as well as for the actual two-electron atom.

3. The First-Order Perturbed Wavefunction for the Two-Electron Atom

The technique suggested by the author for the analytic solution of the two-electron Schrödinger equation is most easily understood when applied to the simpler first-order perturbation equation. The method of solution which may be called the partial series expansion technique of this inhomogeneous partial differential equation will be examined in detail.

In Z-reduced atomic units the Schrödinger equation for the two electron system is

$$\left(H_0 + Z^{-1} V - E \right) \Psi = 0 \tag{89}$$

where $V = r_{12}^{-1}$ and

$$H_0 = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_1} - \frac{1}{r_2} . \tag{90}$$

Expansion of Ψ and E in powers of Z^{-1} is possible

$$\Psi = \Psi_0 + Z^{-1}\Psi_1 + \cdots , \tag{91}$$

$$E = \epsilon_0 + Z^{-1}\epsilon_1 + Z^{-2}\epsilon_2 + Z^{-3}\epsilon_3 + \cdots , \tag{92}$$

the resulting series being convergent for large enough Z.

The zeroth order results are

$$\psi_0 = \pi^{-1} exp \left(-r_1 - r_2 \right) \ , \quad \epsilon_0 = -1 \qquad (93)$$

for the ground state. The first-order perturbed wavefunction
is given by

$$\left(H_0 - \epsilon_0 \right) \psi_1 = \left(\epsilon_1 - V \right) \psi_0 \qquad (94)$$

where $\epsilon_1 = 5/8$. The solution of this equation is unique except
to the extent of an additive multiple of ψ_0 , which can be fixed
by demanding that ψ_1 is orthogonal to ψ_0 .

ψ_1 depends on three variables which are taken to be the
metric variables r_1, r_2, r_{12}.

The ranges of the variables are not independent, but are
governed by the triangular conditions

$$r_1 + r_2 \geqslant r_{12} \geqslant |r_1 - r_2| \ . \qquad (95)$$

Let H_0 be partitioned into two parts

$$H_0 = H_0' + \Lambda \qquad (96)$$

where

$$H_0' = -\frac{1}{2} \left(\frac{1}{r_1} \frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2} \frac{\partial^2}{\partial r_2^2} r_2 \right) - \frac{1}{r_1} - \frac{1}{r_2} \ , \qquad (97)$$

and

$$\Lambda = -\left(\frac{1}{r_{12}} \frac{\partial^2}{\partial r_{12}^2} r_{12} + \frac{2\mathcal{D}}{r_{12}} \frac{\partial}{\partial r_{12}} + 2\mathcal{D}' r_{12} \frac{\partial}{\partial r_{12}} \right) \tag{98}$$

where

$$\mathcal{D} = \frac{1}{4}(r_1^2 - r_2^2)\left(\frac{1}{r_1} \frac{\partial}{\partial r_1} - \frac{1}{r_2} \frac{\partial}{\partial r_2} \right),$$

$$\tag{99}$$

$$\mathcal{D}' = \frac{1}{4}\left(\frac{1}{r_1} \frac{\partial}{\partial r_1} + \frac{1}{r_2} \frac{\partial}{\partial r_2} \right).$$

Equation (94) for ψ_1 may then be written as

$$\left[\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2(\mathcal{D}+1)}{r_{12}} \frac{\partial}{\partial r_{12}} \right) - \left(H_0' - \epsilon_0 - 2\mathcal{D}' r_{12} \frac{\partial}{\partial r_{12}} \right) \right] \psi_1$$

$$= \epsilon_1 \psi_0 - \frac{1}{r_{12}} \psi_0 . \tag{100}$$

Assume that ψ_1 can be expanded as a power series in r_{12} with coefficients which are functions of r_1 and r_2

$$\psi_1 = \sum_{n=0}^{\infty} r_{12}^n \, \varphi_n(r_1, r_2) \tag{101}$$

The series may be begun with the power σ as for the Hooke atom

(equation (12)), but the argument given previously leads to $\sigma = 0$.

Such a solution can certainly be a formal solution to the problem as is shown below. Appendix I explains what is meant by a formal solution to an equation.

Equating coefficients of various powers of r_{12} to zero leads to the set of equations

$$(\mathcal{D} + 1) \, \varphi_1 = \frac{1}{2} \, \psi_0 \, ,$$

(102)

$$(\mathcal{D} + \frac{3}{2}) \, \varphi_2 - \frac{1}{4} (H_0' - \epsilon_0) \, \varphi_0 = -\frac{1}{4} \, \epsilon_1 \psi_0 \, ,$$

(103)

$$\left(\mathcal{D} + \frac{n+1}{2}\right) \varphi_n = \frac{1}{2n} \left(H_0' - \epsilon_0 - 2(n-2)\mathcal{D}' \right) \varphi_{n-2} \, ,$$

(104)

$$n > 2$$

for the φ_n . The same situation arises here as with the Hooke atom, that is φ_0 is not determined by these equations. There is then an arbitrariness in the coefficient of the even powers of r_{12} which can be fixed by requiring ψ_1 to obey the boundary conditions (see equations (22) - (24)).

Put

$$\varphi_0 = c_0 \psi_0 + \varphi_0'$$

(105)

where C_0 is determined by the requirement

$$\langle \psi_1, \psi_0 \rangle = 0 \qquad (106)$$

and φ_0' is determined by requiring ψ_1 to satisfy the boundary conditions. The equations (102) - (104) may now be integrated directly by the introduction of the variables $x = r_1^2 + r_2^2$, $y = r_1^2 - r_2^2$ so that

$$\mathcal{D} = y \frac{\partial}{\partial y} \qquad , \qquad \mathcal{D}' = \frac{\partial}{\partial x} \quad .$$

Equations (102) - (104) become

$$\frac{\partial}{\partial y} (y \varphi_1) = \frac{1}{2} \psi_0 , \qquad (107)$$

$$\frac{\partial}{\partial y} (y^{3/2} \varphi_2) = -\frac{1}{4} \epsilon_1 y^{1/2} \psi_0 + \frac{1}{4} y^{1/2} (H_0' - \epsilon_0) \varphi_0' , \qquad (108)$$

$$\frac{\partial}{\partial y} (y^{\frac{n+1}{2}} \varphi_n) = y^{\frac{n-1}{2}} \left[\frac{1}{2n} (H_0' - \epsilon_0) \right.$$
$$\left. + \left(\frac{2}{n} - 1 \right) \mathcal{D}' \right] \varphi_{n-2} \qquad (109)$$

where

$$H_0' = -2\left[X\frac{\partial^2}{\partial x^2} + 3\frac{\partial}{\partial x} + 2y\frac{\partial^2}{\partial x\partial y} + X\frac{\partial^2}{\partial y^2}\right]$$

$$-\left(\frac{2}{x+y}\right)^{1/2} - \left(\frac{2}{x-y}\right)^{1/2}, \tag{110}$$

$$\psi_0(x,y) = \pi^{-1}\exp\left[-\sqrt{x+\sqrt{x^2-y^2}}\right]. \tag{111}$$

The coefficients of the odd powers of r_{12} may now be determined explicitly by requiring that each term of (101) be square integrable. For φ_1 the result is

$$\varphi_1 = \frac{1}{2}\int_0^1 \psi_0(x,\alpha y)\,d\alpha \tag{112}$$

or

$$\varphi_1 = \frac{1}{2}\psi_0 - \frac{S\eta^2}{4\pi}\int_0^1 (1-k)^{1/2}\exp\left[-S\sqrt{1+k\eta^2}\right]dk \tag{113}$$

where

$$S = r_1 + r_2,$$

$$\tag{114}$$

$$\eta = \frac{r_1 - r_2}{r_1 + r_2}$$

and

$$\alpha^2 = (1-k)(1+k\eta^2) .$$

φ_3 can also be reduced to a single integral and the same appears true for the higher odd coefficients. φ_2 can be written as

$$\varphi_2 = -\frac{1}{4} \epsilon_1 \int_0^1 \alpha^{1/2} \psi_0(x, \alpha y) d\alpha + \varphi_2' \tag{115}$$

where

$$\varphi_2' = \frac{y^{-3/2}}{4} \int_0^y \alpha^{1/2} (H_0' - \epsilon_0) \varphi_0'(x, \alpha) d\alpha . \tag{116}$$

An expansion of each coefficient may be made in powers of η^2 and the first few terms of the first coefficients are

$$\varphi_1 = \frac{1}{2} \psi_0 \left[1 - \frac{1}{3} S\eta^2 + \frac{1}{15} S^2 \eta^4 + \cdots \right] \tag{117}$$

$$\varphi_2 = \varphi_2' - \frac{1}{6} \epsilon_1 \psi_0 \left[1 - \frac{2}{7} S\eta^2 + \frac{2S(2S-1)}{77} \eta^4 + \cdots \right] \tag{118}$$

$$\varphi_3 = \frac{1}{9} \psi_0 \left[\frac{1}{S} - \left(\frac{2}{5} + \left[\frac{7}{8}\right]\frac{1}{S} \right) \eta^2 + \cdots \right] . \tag{119}$$

The coefficients of the even powers of r_{12} are not yet completely determined but the coefficients of the odd powers of r_{12} have no

arbitrariness. A check on the odd coefficients is available. In Appendix E it is shown that if the solution ψ_1 is expanded in a Legendre series in $\cos\theta$ where θ is the angle between the radius vectors $\vec{r}_1$ and $\vec{r}_2$

$$\psi_1 = \psi_0 \sum_{\ell=0}^{\infty} f_\ell(r_1,r_2)\, P_\ell(\cos\theta) \tag{120}$$

then for large ℓ the f_ℓ behave as ℓ^{-2}

$$f_\ell = \frac{f^{(-1)}}{(\ell+\tfrac{1}{2})^2} + \frac{f^{(-2)}}{(\ell+\tfrac{1}{2})^4} + \cdots \tag{121}$$

where the $f^{(-n)}$ can be determined independently of the above series solution.

Equations (46) - (52) demonstrate that the corresponding series solution for the Hooke's law atom leads to the correct values of $f^{(-1)}$ and $f^{(-2)}$ for that model. The same is true for the actual atom, φ_1 and φ_3 above (equations (117) and (119)) directly give the same $f^{(-1)}$ and $f^{(-2)}$ as quoted in Appendix E .

What about φ_0' ? It is known that the first order wavefunction can not be expanded in simple powers of $\rho = \sqrt{r_1^2+r_2^2}$, yet the above expansion with φ_0' absent is just of that type. Thus φ_0' must not be zero. But φ_0' is needed only if the rest of ψ_1 does not satisfy the proper boundary conditions. A more detailed analysis is necessary to discover why ψ_1 with $\varphi_0'=0$ does not satisfy the boundary conditions. In effect a partial summation of

the series for ψ_1 , equation (101), will have to be made.

In order to further investigate the behavior of ψ_1 it is convenient to write equation (109) in terms of the variables S and $\eta^2 = \tau$ (see equation (114)). Let the dependent variable be changed to f_n defined by

$$\varphi_n = e^{-S} f_n .$$

(122)

Then equation (109) becomes

$$-2n \left[\frac{2\tau(1+\tau)}{1-\tau} \frac{\partial}{\partial \tau} - \frac{S\tau}{1-\tau} \frac{\partial}{\partial S} + \frac{S\tau}{1-\tau} \right.$$

$$\left. + \frac{n+1}{2} \right] f_n (S, \tau) = \left[\frac{\partial^2}{\partial S^2} + \frac{4\tau(1+\tau)}{S^2} \frac{\partial^2}{\partial \tau^2} \right.$$

$$- \frac{4\tau}{S} \frac{\partial^2}{\partial S \partial \tau} + \frac{2n}{S(1-\tau)} \frac{\partial}{\partial S} - 2\frac{\partial}{\partial S}$$

$$+ 2 \frac{(1 + 2(1-2n)\tau - 3\tau^2)}{S^2(1-\tau)} \frac{\partial}{\partial \tau} + \frac{4\tau}{S} \frac{\partial}{\partial \tau}$$

$$\left. - \frac{2(n-2)}{S(1-\tau)} \right] f_{n-2} .$$

(123)

A hint of what to expect can be found in the above equation. Notice that ϕ_3 , equation (119), has a term $s^{-1} e^{-s}$. The above equation then will produce a term in ϕ_5 which behaves like $s^{-3} e^{-s}$, in ϕ_7 a term like $s^{-5} e^{-s}$ and in general ϕ_{2m+1} will contain a term like $s^{-2m+1} e^{-s}$. That means that ψ_1 will contain terms like

$$\psi_1 \sim s^2 e^{-s} \sum_n C_n \left(\frac{\mu}{s}\right)^{2m+1} + \cdots \qquad (124)$$

and if $C_n \sim \frac{1}{n}$ for large n this partial sum converges to a term proportional to $\log \left(1 - \frac{\mu^2}{s^2}\right)$ which is divergent at $s = \mu$. This type of term violates the boundary conditions as can be seen from Appendix H .

Anticipation of the above leads to the expansion

$$f_n = \sum_{k=0}^{\infty} f_{nk}(s)\, \gamma^k \, . \qquad (125)$$

Substitution of this expansion into equation (123) and equating the coefficients of the various powers of γ to zero determines f_{nk} as

$$f_{m,k}(S) = \frac{2}{n+4k+1}\left[S\frac{\partial}{\partial S} - S + \frac{n}{2} - 2k + \frac{5}{2}\right]f_{m,k-1}$$

$$- \frac{(k+1)(k+2)}{n(n+4k+1)}\ \frac{f_{n-2,k+1}}{S^2} \qquad (126)$$

$$- \frac{1}{n(n+4k+1)}\left[\frac{\partial^2}{\partial S^2} + \frac{2(n-2k)}{S}\frac{\partial}{\partial S} - 2\frac{\partial}{\partial S}\right.$$

$$\left. - \frac{4k(2n-1)}{S^2} + \frac{2(2k-n+2)}{S}\right]f_{n-2,k}$$

$$+ \frac{1}{n(n+4k+1)}\left[\frac{\partial^2}{\partial S^2} - \frac{4(k-1)}{S}\frac{\partial}{\partial S} - 2\frac{\partial}{\partial S}\right.$$

$$\left. + \frac{(k-1)(k+4)}{S^2} + \frac{4(k-1)}{S}\right]f_{n-2,k-1}$$

where $n \geqslant 3$, $k \geqslant 0$ and the $f_{m,k}$ with negative indices are to be ignored. For $k = 0$ this equation becomes

$$f_{m,0}(S) = -\frac{1}{n(n+1)}\left[\frac{\partial^2}{\partial S^2} + \frac{2n}{S}\frac{\partial}{\partial S} - 2\frac{\partial}{\partial S}\right.$$

$$\left. - \frac{2(n-2)}{S}\right]f_{n-2,0}$$

$$- \frac{2}{n(n+1}\ \frac{f_{n-2,1}}{S^2}\ . \qquad (127)$$

This recursion relation is still too complex to treat easily, but if terms of $O\left(\frac{1}{n^2}\right)$ are dropped the simpler equation

$$f_{n,0}(S) \simeq -\frac{1}{n(n+1)}\left[\frac{\partial^2}{\partial S^2} + \frac{2n}{S}\frac{\partial}{\partial S} - 2\frac{\partial}{\partial S}\right.$$

$$\left. -\frac{2n}{S}\right] f_{n-2,0} \tag{128}$$

is obtained. Since it appears likely that the leading term in behaves like S^{-n+2} for n odd assume

$$f_{n,0}(S) = C_{-n+2,n,0}\, S^{-n+2}$$

$$+ C_{-n+3,n,0}\, S^{-n+3} + \cdots$$

$$n\ \text{odd} \geqslant 3 \tag{129}$$

Substitution of this form for $f_{n,0}$ into both sides of (128) and again dropping all terms of $O\left(\frac{1}{n^2}\right)$ leads to

$$C_{-n+2,n,0} = \left(\frac{n-1}{n+1}\right) C_{-n+4,n-2,0}\ . \tag{130}$$

Relating back to $C_{-1,3,0}$ gives

$$C_{-n+2,n,0} = \frac{4}{n+1} C_{-1,3,0} \qquad (131)$$

for n odd > 3 and where $C_{-1,3,0} = (9\pi)^{-1}$. Thus the odd coefficients may be partially summed

$$\psi_1 \simeq \psi_0 \sum_{\substack{n=3 \\ odd}}^{\infty} \frac{4}{n+1} \left(\frac{s^2}{9}\right) \frac{\mu^n}{s^n} + \cdots \qquad (132)$$

or performing the summation

$$\psi_1 = -\frac{2}{9}\left[s\mu + \frac{s^3}{\mu} \log\left(1 - \frac{\mu^2}{s^2}\right)\right]\psi_0 + \cdots \qquad (133)$$

Other partial summations of ψ_1 can be performed and they lead to similar but non-canceling results. This type of term violates the boundary conditions given in Appendix H. Hence φ_0' is _not_ zero and must cause a cancellation of all such terms in the final result.

By Fock's analysis (see equations (II.51)-(II.60)) φ_0' must contain terms which are logarithmic in the variable $\rho = \sqrt{r_1^2 + r_2^2}$ In fact it is somewhat reassuring to notice that in Fock's method for generating the exact solution, the logarithmic terms in ρ enter only in conjunction with the even powers of μ, in complete agreement with the above analysis.

Except for φ_0' and the subsequent coefficients of the even powers of r_{12} derived from φ_0' the solution ψ_1 is completely

determined. At this point it is not known how to determine $\varphi_0^{'}$ explicitly, but the author feels that $\varphi_0^{'}$ must be determinable and thus that the exact solution of the first-order equation can be realized by this technique.

4. Power Series Solution of the Schrödinger Equation for the Two-
   Electron Atom

The same technique used to obtain the solution to the first-
order perturbation equation for the two-electron atom may be applied
to the complete Schrödinger equation for that system.

In Z-reduced atomic units the Schrödinger equation for the
two-electron atom is

$$\left(H_0 + \lambda\, r_{12}^{-1} - E \right) \Psi = 0 \tag{134}$$

where $\lambda = Z^{-1}$ and

$$H_0 = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2 \right) - \frac{1}{r_1} - \frac{1}{r_2} . \tag{135}$$

As before write

$$H_0 = H_0' + \Lambda \tag{136}$$

where H_0' and Λ are given by equations (97) and (98). Assume
that a solution exists of the form

$$\Psi = \sum_{n=0}^{\infty} r_{12}^{n}\, \phi_n(r_1, r_2) \tag{137}$$

with the ϕ_n to be determined. Substitute (137) into (134) and
use the independence of the powers of r_{12} within the range

$\left(\left| r_1 - r_2 \right|, \; r_1 + r_2 \right)$ to equate the coefficients of the powers of r_{12} to zero. This leads to the set of equations

$$\left(\mathcal{D} + 1 \right) \phi_1 = \frac{\lambda}{2} \phi_0 , \qquad\qquad (138)$$

$$\left(\mathcal{D} + \frac{m+1}{2} \right) \phi_m = \frac{\lambda}{2m} \phi_{m-1}$$

$$+ \left[\frac{1}{2m} \left(H_0' - E \right) + \left(\frac{2}{m} - 1 \right) \mathcal{D}' \right] \phi_{m-2}$$

$$(139)$$

where $\mathcal{D}$ and $\mathcal{D}'$ are given by equation (99).

The key problem is once again the determination of ϕ_0 , because if ϕ_0 is known all the higher ϕ_m can be obtained by inverting the first order partial differential operators appearing on the left side of equations (138) and (139). As before it is not known how to determine ϕ_0 , but if attempts to generate ϕ_0 for the first-order problem should prove successful similar techniques should work here for the total two-electron Schrödinger equation.

Appendix J contains published material on this problem. Note that the second technique, the integral series solution, contains an error in equation (8) and of course also depends on ϕ_0 being known.

Note that, in the case of the lithium atom, where interparticle coordinates can also be used, the obvious generalization of equation (137) to a triply infinite power series in r_{12}, r_{23} and r_{31} leads to an inconsistency (of order λ^2) if only positive powers are allowed.

5. The Series Solution of the Schrödinger Equation for the Hydrogen Molecule.

The non-relativistic Schrödinger equation for the simplest states of the two-electron diatomic molecule with fixed nuclei of atomic number Z_a and Z_b a distance R apart may be treated in much the same manner as the two-electron atom. The Schrödinger equation for the two-electron diatomic molecule is

$$\left(H_0 + \lambda r_{12}^{-1} - E\right)\Psi = 0 \tag{139}$$

where

$$\lambda = 1$$

$$H_0 = h(1) + h(2) \tag{140}$$

and h is the one-electron Hamiltonian

$$h = -\frac{1}{2}\nabla^2 - \frac{Z_a}{r_a} - \frac{Z_b}{r_b}. \tag{141}$$

For Σ states the spatial wavefunction Ψ depends on only five variables which can be taken to be the four electron-nucleus distances r_{a1}, r_{b1}, r_{a2}, r_{b2} and the inter-electron distance r_{12}. Note that the ranges of these variables are interdependent just as with the two-electron atom variables r_1, r_2, r_{12}. H_0 can

be partitioned into two parts in much the same way as was done for the atom (equations (96) and (136)) and can be written as

$$H_0 = H_0' + \Lambda \tag{142}$$

with

$$H_0' = h'(1) + h'(2) \tag{143}$$

and

$$\Lambda = -\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2(\mathcal{D}+1)}{r_{12}} \frac{\partial}{\partial r_{12}} + 2\mathcal{D}' r_{12} \frac{\partial}{\partial r_{12}} \right) \tag{144}$$

where

$$h' = -\frac{1}{2} \left(\frac{\partial^2}{\partial r_a^2} + \frac{2}{r_a} \frac{\partial}{\partial r_a} + \frac{\partial^2}{\partial r_b^2} + \frac{2}{r_b} \frac{\partial}{\partial r_b} \right.$$

$$\left. + \frac{r_a^2 + r_b^2 - R^2}{r_a r_b} \frac{\partial^2}{\partial r_a \partial r_b} \right) - \frac{Z_a}{r_a} - \frac{Z_b}{r_b} , \tag{145}$$

$$\mathcal{D} = \frac{1}{4} \left[(r_{a1}^2 - r_{a2}^2)\left(\frac{1}{r_{a1}} \frac{\partial}{\partial r_{a1}} - \frac{1}{r_{a2}} \frac{\partial}{\partial r_{a2}} \right) \right.$$

$$\left. + (r_{b1}^2 - r_{b2}^2)\left(\frac{1}{r_{b1}} \frac{\partial}{\partial r_{b1}} - \frac{1}{r_{b2}} \frac{\partial}{\partial r_{b2}} \right) \right] \tag{146}$$

$$\mathcal{D}' = \frac{1}{4}\left[\frac{1}{r_{a1}}\frac{\partial}{\partial r_{a1}} + \frac{1}{r_{a2}}\frac{\partial}{\partial r_{a2}} + \frac{1}{r_{b1}}\frac{\partial}{\partial r_{b1}} + \frac{1}{r_{b2}}\frac{\partial}{\partial r_{b2}} \right].$$

(147)

Assume a solution exists of the form[86]

$$\bar{\Psi} = \sum_{n=0}^{\infty} r_{12}^{n}\, \bar{\Phi}_{n}(r_{a1}, r_{a2}, r_{b1}, r_{b2})$$

(148)

where the $\bar{\Phi}_{n}$ are functions of the four variables r_{a1}, r_{a2}, r_{b1}, r_{b2} to be determined. Substituting (148) into (139) and equating coefficients of the powers of r_{12} to zero leads to the equations

$$(\mathcal{D} + 1)\bar{\Phi}_{1} = \frac{\lambda}{2}\bar{\Phi}_{0},$$

(149)

$$\left(\mathcal{D} + \frac{n+1}{2}\right)\bar{\Phi}_{n} = \frac{\lambda}{2n}\bar{\Phi}_{n-1} + \left[\frac{1}{2n}(H_{0}' - E) + \left(\frac{2}{n} - 1\right)\mathcal{D}'\right]\bar{\Phi}_{n-2}$$

$$n = 2, 3, 4, \cdots \quad .$$

(150)

The same difficulty arises here in the determination of $\bar{\Phi}_{0}$, but if $\bar{\Phi}_{0}$ were known the exact solution could be obtained by the inversion of the operators on the left-hand side of equations (149) and (150). Since the operator $\mathcal{D}$ is a first-order partial differential operator this inversion can be accomplished analytically by a single integration. It is hoped that a scheme may be developed for the generation of $\bar{\Phi}_{0}$.

6. The Series Solution for the Two-Electron Atom in the Presence
    of a Uniform Electric Field

The non-relativistic Hamiltonian for a system consisting of

two electrons in the presence of a fixed nucleus and a uniform

electric field[87] (in the z-direction) is, in atomic units

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} + F_0(y_1 + y_2).$$

(151)

If Z-scaled atomic units are used the Schrödinger equation for the

system is

$$\left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}} + F(y_1 + y_2) - E \right] \Psi = 0$$

(152)

where

$$\lambda = Z^{-1}$$

and

$$F = F_0 / Z^3.$$

(153)

Since Ψ depends on five variables which can be taken to be

the four parabolic coordinates

$$\xi_1 = r_1 + y_1,$$

$$\eta_1 = r_1 - y_1,$$

$$\xi_2 = r_2 + y_2,$$ (154)

$$\eta_2 = r_2 - y_2,$$

and the interelectron distance r_{12} , equation (152) may be written as

$$\left(H_0' + \Lambda + \frac{\lambda}{r_{12}} - E \right) \Psi = 0$$ (155)

where

$$H_0' = -\frac{1}{2} \left(\frac{4}{\xi_1 + \eta_1} \frac{\partial}{\partial \xi_1} \xi_1 \frac{\partial}{\partial \xi_1} + \frac{4}{\xi_1 + \eta_1} \frac{\partial}{\partial \eta_1} \eta_1 \frac{\partial}{\partial \eta_1} \right.$$

$$+ \frac{4}{\xi_2 + \eta_2} \frac{\partial}{\partial \xi_2} \xi_2 \frac{\partial}{\partial \xi_2} + \left. \frac{4}{\xi_2 + \eta_2} \frac{\partial}{\partial \eta_2} \eta_2 \frac{\partial}{\partial \eta_2} \right)$$

$$- \frac{2}{\xi_1 + \eta_1} - \frac{2}{\xi_2 + \eta_2} + \frac{F}{2} \left(\xi_1 - \eta_1 + \xi_2 - \eta_2 \right),$$

(156)

$$\Lambda = -\left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{2\mathscr{D}}{r_{12}}\frac{\partial}{\partial r_{12}} + 2\mathscr{D}'r_{12}\frac{\partial}{\partial r_{12}}\right),$$

$$(157)$$

$$\mathscr{D} = \frac{1}{4}\left(\xi_1 - \eta_1 - \xi_2 + \eta_2\right)\left(\frac{\partial}{\partial \xi_1} - \frac{\partial}{\partial \eta_1} - \frac{\partial}{\partial \xi_2} + \frac{\partial}{\partial \eta_2}\right)$$

$$+ \frac{1}{8}\frac{(\xi_1 + \eta_1)^2 - (\xi_2 + \eta_2)^2}{(\xi_1 + \eta_1)}\left(\frac{\partial}{\partial \xi_1} + \frac{\partial}{\partial \eta_1}\right)$$

$$+ \frac{1}{8}\frac{(\xi_2 + \eta_2)^2 - (\xi_1 + \eta_1)^2}{(\xi_2 + \eta_2)}\left(\frac{\partial}{\partial \xi_2} + \frac{\partial}{\partial \eta_2}\right),$$

$$(158)$$

and

$$\mathscr{D}' = \frac{1}{2}\left[\frac{1}{\xi_1 + \eta_1}\left(\frac{\partial}{\partial \xi_1} + \frac{\partial}{\partial \eta_1}\right) + \frac{1}{\xi_2 + \eta_2}\left(\frac{\partial}{\partial \xi_2} + \frac{\partial}{\partial \eta_2}\right)\right].$$

$$(159)$$

Expansion of Ψ as a power series in the interelectron distance r_{12}

$$\Psi = \sum_{n=0}^{\infty} r_{12}^n \phi_n(\xi_1, \eta_1, \xi_2, \eta_2) \qquad (160)$$

with coefficients ϕ_n which are functions of the four variables $\xi_1, \eta_1, \xi_2, \eta_2$ and substitution of this form for Ψ into

(155) leads to the set of equations

$$\left(\mathcal{D} + 1\right)\phi_1 = \frac{\lambda}{2}\,\phi_0 \,, \tag{161}$$

$$\left(\mathcal{D} + \frac{n+1}{2}\right)\phi_n = \frac{\lambda}{2n}\,\phi_{n-1} + \left[\frac{1}{2n}\left(H_0' - E\right) + \left(\frac{2}{n} - 1\right)\mathcal{D}'\right]\phi_{n-2}, \quad n \geqslant 2 \tag{162}$$

to determine the ϕ_n. The same difficulty concerning ϕ_0 is encountered here, but with ϕ_0 known the first order differential operators on the left of (161) and (162) can be inverted analytically to give all higher ϕ_n explicitly.

IV. CONCLUSION: WHY NOT ϕ_0 ?

The growth in interest in two-electron systems over the past
few years has been truly phenomenal, as evidenced by Appendix K
which concerns only the ground state of the two-electron atom. If
an analytic solution to the Schrödinger equation is to be realized
for this system it is felt that the technique presented in this
thesis is the means by which that realization will take place.
The defect in the analysis presented here is that the "starting
function", ϕ_0 , from which the solution is generated is, at
present, unknown. It is hoped that some new approach to the problem
is possible which will yield an actual equation for this function
ϕ_0 . Since, for the ground state, ϕ_0 is a function of only
two variables this equation woild be only two-dimensional. In
conclusion, then, the author feels that attention should be
concentrated on the determination of ϕ_0 for herein lies the
key to the complete analytic solution of the Schrödinger equation
for both the two-electron atom and the two-electron diatomic
molecule.

Appendix A - The Variational Theorem

As is well known, the Schrödinger equation

$$(H - E)\Psi = 0 \tag{1}$$

is completely equivalent to the variational principle which states that Ψ and E are given by

$$\delta \tilde{E} = 0 \tag{2}$$

where

$$\tilde{E} = \frac{\langle \Psi, H\Psi \rangle}{\langle \Psi, \Psi \rangle}$$

and where the variation is with respect to any arbitrary functional variation $\delta \Psi$. This variation principle leads to the variational theorem

$$\tilde{E} = \frac{\langle \Psi, H\Psi \rangle}{\langle \Psi, \Psi \rangle} \geq E \tag{3}$$

where E is the lowest eigenvalue of H and Ψ is any function in the domain of H . Equality is obtained only for $\Psi = \Psi$, the exact ground state eigenfunction. Actually, a much more general statement holds, but since all work in this thesis concerns the ground state the above is adequate.

In practice,[88] parameters are embedded in some trial function ψ, the functional $\tilde{E}$, equation (3), it computed and finally the parameters are chosen to make $\tilde{E}$ a minimum. This minimum is then an upper limit to the true ground state energy.

Two types of trial functions are common and are often used simultaneously. The most convenient form to use for ψ is that of a linear combination of basis functions. Suppose that a trial function of the form

$$\psi = \sum_{i=1}^{N} c_i \varphi_i \tag{4}$$

is assumed, where the φ_i are some convenient set of basis elements in the domain of H and the c_i are constants to be determined by the minimum energy requirement

$$\frac{\partial \tilde{E}}{\partial c_i} = 0 \quad , \quad i = 1, 2, \cdots, N. \tag{5}$$

Substitution of equation (4) into equation (3) followed by minimization leads to a determinantal equation of the form

$$\det \left\{ \underline{H} - \tilde{E} \, \underline{\underline{S}} \right\} = 0 \tag{6}$$

where $\underline{\underline{H}}$ is the matrix with elements

$$H_{ij} = \langle \varphi_i, H \varphi_j \rangle \tag{7}$$

and $\underset{\sim}{S}$ is the overlap matrix

$$S_{ij} = \langle \varphi_i, \varphi_j \rangle.$$ (8)

The lowest root of this equation is the best upper bound on E obtainable with the particular basis set using only linear parameters.

A second type of parameter may be introduced into the problem. This is the scale parameter and is non-linear. If too many non-linear parameters are used, the calculation becomes unwieldy, so only a uniform scale will be considered here. Usually the Hamiltonian is of the form

$$H = T + U$$ (9)

where the kinetic energy, T, is homogeneous of degree -2 and the potential energy, U, is homogeneous of degree minus one. Let all coordinates in a trial wavefunction be scaled uniformly by ζ, where ζ is to be determined. Equation (3) becomes

$$\zeta^2 \mathcal{K}(1) + \zeta \mathcal{U}(1) - \tilde{E} = 0$$ (10)

where

$$\mathcal{K}(1) = \frac{\langle \psi, T\psi \rangle}{\langle \psi, \psi \rangle}\Bigg|_{\zeta=1},$$

and

$$U(1) = \left. \frac{\langle \psi, U\psi \rangle}{\langle \psi, \psi \rangle} \right|_{\eta=1} .$$

Minimization of $\tilde{E}$ with respect to η leads to

$$\tilde{E}_{min} = - \frac{U^2(1)}{4 K(1)} , \tag{11}$$

and

$$\eta_{min} = - \frac{U(1)}{2 K(1)} \tag{12}$$

The wavefunction thus minimized satisfies the virial theorem.[89]

In practice, for large basis sets, either no variation in the scale parameter is allowed[47] or else some type of relaxation technique[36] is used to obtain η_{min}.

Appendix B. Coordinate Systems for Ground State Calculations

Various coordinate systems have been suggested or used for calculations involving the two-electron atom in its ground state. This Appendix gives the form of the relevant quantities for all of the commonly used coordinates. The form of $(\nabla_1 \psi)^2 + (\nabla_2 \psi)^2$ is given because this is the way the kinetic energy is usually written when using the variational theorem. By Green's theorem

$$\langle \psi, (\nabla_1^2 + \nabla_2^2)\psi \rangle = - \langle 1, (\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 \rangle \tag{1}$$

when the surface term vanishes. That the surface term must vanish is a consequence of the natural boundary conditions associated with the Hermitian property of the energy.

$$(r_1, r_2, \theta) \tag{2}$$

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{r_1} \frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2} \frac{\partial^2}{\partial r_2^2} r_2$$

$$+ \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}$$

$$(\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 = \left(\frac{\partial \psi}{\partial r_1}\right)^2 + \left(\frac{\partial \psi}{\partial r_2}\right)^2$$

$$+ \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\left(\frac{\partial \psi}{\partial \theta}\right)^2,$$

$$\langle \psi, \psi \rangle = 8\pi^2 \int_0^\infty dr_1 \int_0^\infty dr_2 \int_0^\pi d\theta \; r_1^2 \, r_2^2 \, \sin\theta \, |\psi|^2.$$

$$(r_1, r_2, r_{12}) \tag{3}$$

$$r_{12}^2 = r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta,$$

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{r_1}\frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2} r_2 + \frac{2}{r_{12}}\frac{\partial^2}{\partial r_{12}^2} r_{12}$$

$$+ \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}},$$

$$(\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 = \left(\frac{\partial \psi}{\partial r_1}\right)^2 + \left(\frac{\partial \psi}{\partial r_2}\right)^2 + 2\left(\frac{\partial \psi}{\partial r_{12}}\right)^2$$

$$+ \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}}\left(\frac{\partial \psi}{\partial r_1}\right)\left(\frac{\partial \psi}{\partial r_{12}}\right) + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}}\left(\frac{\partial \psi}{\partial r_2}\right)\left(\frac{\partial \psi}{\partial r_{12}}\right),$$

$$\langle \psi, \psi \rangle = 8\pi^2 \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_{12} \; r_1 \, r_2 \, r_{12} \, |\psi|^2.$$

(s,t,u)-Hylleraas Coordinates[12] (4)

$$S = r_1 + r_2,$$
$$t = r_1 - r_2,$$
$$u = r_{12},$$

$$\nabla_1^2 + \nabla_2^2 = 2\frac{\partial^2}{\partial s^2} + 2\frac{\partial^2}{\partial t^2} + 2\frac{\partial^2}{\partial u^2} + \frac{4s(u^2-t^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial s\partial u}$$

$$+ \frac{4t(s^2-u^2)}{u(s^2-t^2)}\frac{\partial^2}{\partial u\partial t} + \frac{4}{u}\frac{\partial}{\partial u} + \frac{8s}{s^2-t^2}\frac{\partial}{\partial s}$$

$$- \frac{8t}{s^2-t^2}\frac{\partial}{\partial t},$$

$$(\nabla_1\psi)^2 + (\nabla_2\psi)^2 = 2\left(\frac{\partial\psi}{\partial s}\right)^2 + 2\left(\frac{\partial\psi}{\partial t}\right)^2 + 2\left(\frac{\partial\psi}{\partial u}\right)^2$$

$$+ \frac{4s(u^2-t^2)}{u(s^2-t^2)}\left(\frac{\partial\psi}{\partial s}\right)\left(\frac{\partial\psi}{\partial u}\right)$$

$$+ \frac{4t(s^2-u^2)}{u(s^2-t^2)}\left(\frac{\partial\psi}{\partial t}\right)\left(\frac{\partial\psi}{\partial u}\right),$$

$$\langle\psi,\psi\rangle = \pi^2\int_0^\infty ds\int_{-s}^{+s}dt\int_{|t|}^{s}du\, u(s^2-t^2)|\psi|^2$$

$$= \pi^2\int_0^\infty du\int_u^\infty ds\int_{-u}^{+u}dt\, u(s^2-t^2)|\psi|^2.$$

(X_1, X_2, X_3) - Gronwall's Coordinates[59,60]   (5)

$$X_1 = \frac{1}{2} r_1 r_2 \cos\theta, \qquad\qquad r_1 = \sqrt{2(r + X_2)},$$

$$X_2 = \frac{1}{4}(r_1^2 - r_2^2), \qquad\qquad r_2 = \sqrt{2(r - X_2)},$$

$$X_3 = \frac{1}{2} r_1 r_2 \sin\theta, \qquad\qquad r_{12} = 2\sqrt{r - X_1},$$

$$r = \sqrt{X_1^2 + X_2^2 + X_3^2} = \frac{1}{4}(r_1^2 + r_2^2),$$

$$\nabla_1^2 + \nabla_2^2 = r\left(\frac{\partial^2}{\partial X_1^2} + \frac{\partial^2}{\partial X_2^2} + \frac{\partial^2}{\partial X_3^2} + \frac{1}{X_3}\frac{\partial}{\partial X_3}\right),$$

$$(\nabla_1\psi)^2 + (\nabla_2\psi)^2 = r\left(\left(\frac{\partial\psi}{\partial X_1}\right)^2 + \left(\frac{\partial\psi}{\partial X_2}\right)^2 + \left(\frac{\partial\psi}{\partial X_3}\right)^2\right),$$

$$\langle\psi,\psi\rangle = 16\pi^2 \int_{-\infty}^{\infty} dX_1 \int_{-\infty}^{\infty} dX_2 \int_{0}^{\infty} dX_3 \; \frac{X_3}{r} |\psi|^2.$$

(ρ, α, θ) - Fock's Coordinates[66] (6)

$$\rho = \sqrt{r_1^2 + r_2^2}, \qquad\qquad r_1 = \rho \cos \frac{\alpha}{2},$$

$$\tan \frac{\alpha}{2} = \frac{r_2}{r_1}, \qquad\qquad r_2 = \rho \sin \frac{\alpha}{2},$$

$$r_{12} = \rho \sqrt{1 - \sin\alpha \cos\theta},$$

$$\nabla_1^2 + \nabla_2^2 = \frac{\partial^2}{\partial \rho^2} + \frac{5}{\rho} \frac{\partial}{\partial \rho}$$

$$+ \frac{4}{\rho^2 \sin^2\alpha} \left(\frac{\partial}{\partial \alpha} \sin^2\alpha \frac{\partial}{\partial \alpha} + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} \right),$$

$$(\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 = \left(\frac{\partial \psi}{\partial \rho} \right)^2 + \frac{4}{\rho^2} \left(\frac{\partial \psi}{\partial \alpha} \right)^2 + \frac{4}{\rho^2 \sin^2\alpha} \left(\frac{\partial \psi}{\partial \theta} \right)^2,$$

$$\langle \psi, \psi \rangle = \pi^2 \int_0^\infty d\rho \int_0^\pi d\alpha \int_0^\pi d\theta \, \rho^5 \sin^2\alpha \, \sin\theta \, |\psi|^2.$$

(X, y, Z) — Pekeris Coordinates[37]   (7)

$$X = r_2 - r_1 + r_{12},$$
$$y = r_1 - r_2 + r_{12},$$
$$Z = 2(r_1 + r_2 - r_{12}),$$

$$r_1 = \tfrac{1}{2}(y + \tfrac{1}{2}Z),$$
$$r_2 = \tfrac{1}{2}(X + \tfrac{1}{2}Z),$$
$$r_{12} = \tfrac{1}{2}(X + y),$$

$$\nabla_1^2 + \nabla_2^2 = \frac{4}{(X + \tfrac{1}{2}Z)(y + \tfrac{1}{2}Z)(X + y)} \left(X\left[(X+y)(y+Z) + \tfrac{1}{2}Z^2\right]\frac{\partial^2}{\partial X^2} \right.$$

$$+ y\left[(X+y)(X+Z) + \tfrac{1}{2}Z^2\right]\frac{\partial^2}{\partial y^2}$$

$$+ Z\left[2(X^2 + y^2) + (X+y)Z\right]\frac{\partial^2}{\partial Z^2}$$

$$- 2XZ(X + \tfrac{1}{2}Z)\frac{\partial^2}{\partial X \partial Z} - 2yZ(y + \tfrac{1}{2}Z)\frac{\partial^2}{\partial y \partial Z}$$

$$+ \left[(X+y)(y+Z) - X^2 + \tfrac{1}{2}Z^2 + Xy - Xy(X+y+Z)\right]\frac{\partial}{\partial X}$$

$$+ \left[(X+y)(X+Z) - y^2 + \tfrac{1}{2}Z^2 + Xy - Xy(X+y+Z)\right]\frac{\partial}{\partial y}$$

$$+ \left.\left[2X^2 + 2y^2 - Z^2 - Z(X^2 + y^2) - \tfrac{Z^2}{2}(X+y)\right]\frac{\partial}{\partial Z} \right),$$

$$(\nabla_1 \psi)^2 + (\nabla_2 \psi)^2 = \frac{4}{(x+\frac{1}{2}z)(y+\frac{1}{2}z)(x+y)} \left(x \left[(x+y)(y+z) + \frac{1}{2} z^2 \right] \left(\frac{\partial \psi}{\partial x} \right)^2 \right.$$

$$+ y \left[(x+y)(x+z) + \frac{1}{2} z^2 \right] \left(\frac{\partial \psi}{\partial y} \right)^2$$

$$+ z \left[2(x^2 + y^2) + (x+y) z \right] \left(\frac{\partial \psi}{\partial z} \right)^2$$

$$- 2xz \left[x + \frac{1}{2} z \right] \left(\frac{\partial \psi}{\partial x} \right) \left(\frac{\partial \psi}{\partial z} \right)$$

$$\left. - 2yz \left[y + \frac{1}{2} z \right] \left(\frac{\partial \psi}{\partial y} \right) \left(\frac{\partial \psi}{\partial z} \right) \right),$$

$$\langle \psi, \psi \rangle = \frac{\pi^2}{8} \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \, (x+y)(x+\tfrac{1}{2}z)(y+\tfrac{1}{2}z) |\psi|^2.$$

A certain nomenclature has arisen which identifies the type of basis set used in a variational calculation for the two-electron atom. This nomenclature is as follows:

Hylleraas type expansion - Basis set consists of positive integral powers of s,t,u

$$S^n \, \mu^\ell \, t^m \quad , \quad n,\ell,m \geqslant 0.$$

Kinoshita type expansion - Basis set consists of positive and negative integral powers of s and u, positive integral powers of t

$$S^{n-\ell} \, \mu^{\ell-m} \, t^m \quad , \quad n,\ell,m \geqslant 0.$$

C. Schwartz type - Basis set consists of positive integral and half-integral powers of s, positive integral powers of u and t

$$S^{\frac{n}{2}} \, \mu^\ell \, t^m \quad , \quad n,\ell,m \geqslant 0.$$

H. M. Schwartz type - Basis set consists of positive integral and half-integral powers of s and u, positive integral powers of t

$$S^{n/2} \, \mu^{\ell/2} \, t^m \quad , \quad n,\ell,m \geqslant 0.$$

Appendix C. Lower Bounds for Energy Eigenvalues

The traditional Rayleigh-Ritz variational principle (see

Appendix A) furnishes a convenient method of obtaining upper bounds

to the exact energy of the ground state of a system of interest, but

lower bounds are much more difficult to obtain. Three basic

techniques have been used in calculating lower bounds for small

systems. These three techniques are

1. The Stevenson Variational Technique,

2. The Method of Intermediate Hamiltonians,

3. The Bracketing Theorem of Löwdin.

The oldest method, the Stevenson[90,91] variational technique,

begins by a consideration of the inequality

$$\frac{\langle \psi, (H-E_0)(H+E_0-2\alpha)\psi \rangle}{\langle \psi, \psi \rangle} \geq 0 \tag{1}$$

where

$$E_0 \leq \alpha \leq \frac{1}{2}(E_0 + E_1) \tag{2}$$

and E_0 and E_1 are the exact energies of the ground state and

first excited state with the same symmetry as the ground state.

ψ is any wave function in the domain of H . Rearrangement of

equation (1) leads to

$$E_0 \geqslant \alpha - \sqrt{\frac{\langle \psi, H^2\psi\rangle}{\langle \psi,\psi\rangle} - 2\alpha \frac{\langle \psi, H\psi\rangle}{\langle \psi,\psi\rangle} + \alpha^2} \qquad (3)$$

which is the Stevenson formula for a lower bound. Note that when

$$\alpha = \frac{\langle \psi, H\psi\rangle}{\langle \psi_1,\psi\rangle} \qquad (4)$$

this becomes Weinstein's formula[92], and when

$$\alpha = \frac{1}{2}(E_0 + E_1) \qquad (5)$$

equation (3) becomes, upon rearrangement, Temple's formula[93].

The procedure usually followed in the use of this formula is to pick an α satisfying equation (2) and then to minimize the functional

$$F = \frac{\langle \psi, H^2\psi\rangle}{\langle \psi,\psi\rangle} - 2\alpha \frac{\langle \psi, H\psi\rangle}{\langle \psi,\psi\rangle} . \qquad (6)$$

This is repeated with various α until the best lower bound is found. Two objections with this technique are often raised (1) E_1 or a lower bound to E_1 must be known, and (2) matrix elements of H^2 must be calculated.

The second technique, the method of intermediate Hamiltonians, is of more recent origin[94]. Generally speaking, a set of operators $H^{(m)}$ is constructed such that

$$H^{(1)} \leqq H^{(2)} \leqq \cdots \leqq H \qquad (7)$$

holds. Then the associated eigenvalues satisfy the same type of inequality

$$E^{(1)} \leqq E^{(2)} \leqq \cdots \leqq E \qquad (8)$$

where $E^{(1)}$, $E^{(2)}$, $\cdots$ E represent the ground state energy of the corresponding Hamiltonians. There are several modifications of this technique which will not be described here. Although the results appear very good, the method has never been pushed to the same accuracy as in upper bound calculations.

Löwdin[95,98] has recently developed a method which produces lower bounds by a somewhat different technique. A partitioning technique is used by means of which the Hilbert space is divided into two subspaces one of which is a one-dimensional space associated with a reference function. A reduced resolvent is defined as

$$T = \frac{P}{\mathcal{E} - H} \qquad (9)$$

where P is the projection operator for the orthogonal complement to the reference function, $\mathcal{E}$ is a variable, and H is the Hamiltonian for the system. Löwdin then defined a "bracketing function"

$$\varepsilon_1 = f(\varepsilon) = \frac{\left\langle \phi, \left(H + H\frac{P}{\varepsilon-H}H\right)\phi\right\rangle}{\left\langle \phi, \phi\right\rangle} \qquad (10)$$

where ϕ is the reference function. The bracketing function has

the property that the interval $(\varepsilon_1, \varepsilon)$ contains at least one true

eigenvalue of H . The technique thus yields lower bounds if ε

is an upper bound. The results are encouraging.

A comparison of the results obtained by the various methods

is given for the ground state of helium in Table 3.

Appendix D.   Perimetric Coordinates for Four Particles

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Perimetric Coordinates for Four Particles

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In a recent article Rasiel and Karl [1] explored the possibility of introducing coordinates $\{u_i\}$ for four particles which would be similar in nature to the three-particle perimetric coordinates introduced by Pekeris [2]. Their conjecture was that these coordinates do not exist for four particles.

If the notation of Rasiel and Karl [1] is used,

$$R = B\,U \tag{1}$$

where

$$R = \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_{12} \\ r_{13} \\ r_{23} \end{pmatrix}, \qquad U = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix}$$

and the $\{u_i\}$ are the coordinates sought, then the conditions on the B matrix set forth by Rasiel and Karl [1] can be fulfilled.

A matrix B which obeys these conditions is

$$B = \begin{pmatrix} 1 & 0 & 1 & 0 & 2 & 2 \\ 0 & 0 & 1 & 3 & 3 & 1 \\ 0 & 1 & 1 & 2 & 0 & 2 \\ 1 & 0 & 0 & 3 & 1 & 3 \\ 1 & 1 & 0 & 2 & 2 & 0 \\ 0 & 1 & 0 & 1 & 3 & 3 \end{pmatrix}, \tag{2}$$

If this matrix is inverted to obtain the $\{u_i\}$ in terms of the $\{r$'s$\}$ it is found that the $\{u_i\}$ do not range from zero to infinity. This introduces a contradiction since the $\{u_i\}$ were assumed to range from zero to infinity in deriving the conditions which B must fulfill.

The conclusion is reached that the requirements on B, as set forth by Rasiel and Karl [1], are not sufficient to determine the transformation.

If the **B** matrix given by RASIEL and KARL as an "almost" perimetric transformation is inverted, it is again found that the $\{u_i\}$ do not range from zero to infinity.

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Appendix E. Angular Correlation in the Helium Atom

Angular Correlation in the Helium Atom

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Schwartz has shown that if the wave function for the ground state of He is developed as a perturbation series in powers of $1/Z$ and if the first-order wave function is expanded in a series of Legendre polynomials in the angle θ between the position vectors of the electrons, the contribution of the P_l component to the second-order energy behaves as l^{-4} for large l. This same behavior is noted for a model atomic system.

THE relative importance of the various angular contributions to the second-order energy for the ground state of the helium atom where $1/Z$ provides a natural perturbation parameter has been discussed by Schwartz.[1,2] He has reported that if the first-order wave function is expanded in a series of Legendre polynomials in the angle θ between the position vectors of the electrons; the contribution of the P_l component to the second-order energy behaves as l^{-4} for large l. Lakin[3] has extended the result to the total energy. This same behavior is obtained for a model atomic system.

The model atomic system will be called the Hooke's law atom. It has been studied previously by Kestner and Sinanoglu[4] and, using perturbation theory, by White and Byers Brown.[5] In this model the electron-nucleus interaction is assumed to be harmonic while the electron-electron interaction remains Coulombic.

For both the actual helium atom and the Hooke's law model, the equation to be solved is

$$(H_0 - E_0)\psi_1 = -(V - E_1)\psi_0, \qquad (1)$$

where $V = 1/r_{12}$. Writing

$$\psi_1 = F\psi_0 \qquad (2)$$

in both cases and expanding F in a Legendre series in the angle θ between the two electrons

$$F = \sum_{l=0}^{\infty} f_l(r_1, r_2) P_l(\cos\theta) \qquad (3)$$

reduces the problem to an infinite set of two-dimensional equations. In both cases the equation which determines f_l is

$$\left[\nabla_1^2 + \nabla_2^2 + \frac{\partial \ln\psi_0^2}{\partial r_1}\frac{\partial}{\partial r_1} + \frac{\partial \ln\psi_0^2}{\partial r_2}\frac{\partial}{\partial r_2}\right] f_l$$
$$= 2\left[\frac{r_<^l}{r_>^{l+1}} - E_1\delta_{l0}\right], \qquad (4)$$

$$\nabla^2 \to \frac{1}{r}\frac{\partial^2 r}{\partial r^2} - \frac{l(l+1)}{r^2}.$$

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For the helium atom

$$\psi_0 = \pi^{-1}\exp[-(r_1+r_2)],$$
$$E_1 = 5/8; \tag{5}$$

for the Hooke's law atom

$$\psi_0 = \pi^{-3/2}\exp[-\tfrac{1}{2}(r_1^2+r_2^2)],$$
$$E_1 = (2/\pi)^{1/2}. \tag{6}$$

Now E_2 can be expanded as

$$E_2 = \sum_{l=0}^{\infty} E_2(l), \tag{7}$$

where

$$E_2(l) = \int \psi_0^2 \frac{r_<^l}{r_>^{l+1}} f_l \frac{dv_1 dv_2}{(2l+1)}, \quad l>0. \tag{8}$$

By changing to the variables

$$s = r_1+r_2,$$
$$y = \frac{|r_2-r_1|}{r_1+r_2}\lambda^{1/2},$$
$$\lambda = (l+\tfrac{1}{2})^2, \tag{9}$$

one obtains the equation for f_l:

$$\left[s^2\frac{\partial^2}{\partial s^2} - 2sy\frac{\partial^2}{\partial s\partial y} + y^2\frac{\partial^2}{\partial y^2} + 2y\frac{\partial}{\partial y} - \alpha s^2\frac{\partial}{\partial s} + \beta s y\frac{\partial}{\partial y} + \lambda\frac{\partial^2}{\partial y^2} \right.$$
$$\left. - \frac{4}{(1-y^2/\lambda)}\left(2y\frac{\partial}{\partial y} - s\frac{\partial}{\partial s}\right) - \frac{4(\lambda-\tfrac{1}{4})(1+y^2/\lambda)}{(1-y^2/\lambda)^2} \right] f_l$$
$$= \frac{2se^{-2y}\exp[-(2y^3/3\lambda)-(2y^5/5\lambda^2)-\cdots]}{(1-y^2/\lambda)^{1/2}}, \tag{10}$$

where

$$\begin{aligned}
\alpha &= 2, &&\text{He} \\
&= s, &&\text{Hooke atom,} \\
\beta &= 2, &&\text{He} \\
&= 0, &&\text{Hooke atom}
\end{aligned} \tag{11}$$

and where the boundary condition

$$\left.\frac{\partial f_l}{\partial y}\right|_{y=0} = 0 \tag{12}$$

must be applied to f_l since it is a symmetric function of r_1, r_2. If f_l is expanded in inverse powers of λ

$$f_l = \lambda^{-1}f^{(-1)} + \lambda^{-2}f^{(-2)} + \cdots, \tag{13}$$

Eq. (10) can be solved to give the following results:

$$f^{(-1)} = -\tfrac{1}{4}se^{-2y}(1+2y) \tag{14}$$

for both the helium atom and the Hooke's law atom and

$$f^{(-2)} = -\tfrac{1}{4}se^{-2y}[(-\tfrac{4}{3}y^4+\tfrac{1}{3}y^3+\tfrac{3}{2}y^2+2y+1)$$
$$-s(\tfrac{2}{3}y^3+y^2+y+\tfrac{1}{2})] \tag{15}$$

for the helium atom,

$$f^{(-2)} = -\tfrac{1}{4}se^{-2y}[(-\tfrac{4}{3}y^4+\tfrac{1}{3}y^3+\tfrac{3}{2}y^2+2y+1)$$
$$-s^2(\tfrac{1}{4}y^2+\tfrac{3}{8}y+\tfrac{3}{16})] \tag{16}$$

for the Hooke's law atom.

The expansion $E_2(l)$ as a power series in λ^{-1} is

$$E_2(l) = -\frac{45}{256}\frac{1}{(l+\tfrac{1}{2})^4}\left[1 - \frac{5/4}{(l+\tfrac{1}{2})^2} + O\!\left(\frac{1}{l^4}\right)\right] \tag{17}$$

for He and

$$E_2(l) = -\frac{3}{4\pi}\frac{1}{(l+\tfrac{1}{2})^4}\left[1 - \frac{5/4}{(l+\tfrac{1}{2})^2} + O\!\left(\frac{1}{l^4}\right)\right] \tag{18}$$

for the Hooke's law atom.

The results reported here differ from those of Schwartz[2] in Eq. (15) and the second term of Eq. (17).

The similarity between the Hooke's law atom and helium indicated by Eqs. (17) and (18), and by Eq. (14), shows that the asymptotic form of f_l is independent of the nature of the electron-nucleus interaction and depends only on the Coulombic electron-electron repulsion. In the case of the Hooke's law atom, F can be obtained analytically[5] and is a function of r_{12} only.

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Appendix F. A Refutation of Bartlett's Argument for Logarithmic Terms

To begin with, the essence of Bartlett's argument[62] will be given in coordinates and notation more convenient than that of the original work. Then a counter argument will be presented in the last part of this Appendix.

The Schrödinger equation for the ground state of the two-electron atom in Z-reduced units may be written as

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial \rho^2} + \frac{5}{\rho}\frac{\partial}{\partial \rho} + \frac{4}{\rho^2}\square^* \right) - \frac{\mu_0}{\rho} + \frac{\lambda \nu_0}{\rho} - E \right]\Psi = 0 \qquad (1)$$

where

$$\square^* = \frac{1}{\sin^2\alpha}\left(\frac{\partial}{\partial\alpha} \sin^2\alpha \frac{\partial}{\partial\alpha} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \right), \qquad (2)$$

$$\mu_0 = \sec\frac{\alpha}{2} + \csc\frac{\alpha}{2}, \qquad (3)$$

$$\nu_0 = \left(1 - \sin\alpha \cos\theta \right)^{-1/2}, \qquad (4)$$

and where the coordinates are those of Fock (see Appendix B). As is pointed out in Appendix G the operator $\square^*$ possesses an orthonormal set of eigenfunctions, $Z_{n\ell}$.

If Ψ is expanded in terms of these eigenfunctions, which form a complete set in the variables α, θ

$$\Psi = \sum_{n=0}^{\infty} \sum_{\ell=0}^{n} \Phi_{n,\ell}(\rho) Z_{n,\ell}(\alpha, \theta) \qquad (5)$$

and this form substituted into equation (1), the result is

$$\sum_{n=0}^{\infty} \sum_{\ell=0}^{n} \left[Z_{n,\ell} \left(-\frac{1}{2} \left(\frac{d^2}{d\rho^2} + \frac{5}{\rho} \frac{d}{d\rho} - 4 \frac{n(n+2)}{\rho^2} \right) \right. \right. \qquad (6)$$

$$\left. \left. - \mu_0 \rho^{-1} + \lambda N_0 \rho^{-1} - E \right) \Phi_{n,\ell} \right] = 0.$$

Multiplication of this equation by $Z_{m,k}$ and integration over all angles leads to the following set of ordinary differential equations for $\Phi_{m,k}$

$$\left[-\frac{1}{2} \left(\frac{d^2}{d\rho^2} + \frac{5}{\rho} \frac{d}{d\rho} - 4 \frac{m(m+2)}{\rho^2} \right) - E \right] \Phi_{m,k}$$

$$- \frac{1}{\rho} \sum_{n=k}^{\infty} A_n^{(m,k)} \Phi_{n,k} + \frac{\lambda}{\rho} \sum_{n=0}^{\infty} \sum_{\ell=0}^{n} B_{n,\ell}^{(m,k)} \Phi_{n,\ell} = 0,$$

$$m = 0, 1, 2, \cdots .$$
$$k = 0, 1, \cdots, m$$
$$(7)$$

where

$$A_n^{(m,k)} = \frac{2}{\pi} \int_0^{\pi} \sin^2 \alpha \, \overline{\Pi_{n,k}} \, \mu_0 \, \Pi_{m,k} \, d\alpha \qquad (8)$$

(See Appendix G for a definition of the $\Pi_{n,k}$.)

and

$$B_{n,\ell}^{(m,k)} = \int_0^\pi d\alpha \int_0^\pi d\theta \, \sin^2\alpha \cos\theta \, Z_{n,\ell} \, Z_{m,k} \, N_0 \, . \tag{9}$$

Bartlett then introduced as a new dependent variable

$$F_{m,k} = \rho^{5/2} \, \Phi_{m,k} \tag{10}$$

which satisfies the following equation

$$\left[\frac{d^2}{d\rho^2} - \left(4m(m+2) + \frac{15}{4} \right) \frac{1}{\rho^2} + 2E \right] F_{m,k}$$

$$+ \frac{2}{\rho} \sum_{m=k}^\infty A_m^{(m,k)} F_{m,k} - \frac{2\lambda}{\rho} \sum_{n=0}^\infty \sum_{\ell=0}^n B_{n,\ell}^{(m,k)} F_{n,\ell} = 0 \tag{11}$$

The definition

$$P_{m,k} = \frac{d}{d\rho} F_{m,k} \tag{12}$$

converts this coupled second order ordinary differential equation into the set of coupled first order ordinary differential equations

$$\frac{d F_{m,k}}{d\rho} = P_{m,k} \, , \tag{13a}$$

$$\frac{dP_{m,k}}{d\rho} = \left(\frac{\gamma_m}{\rho^2} - 2E - \frac{2 A_m^{(m,k)}}{\rho} + \frac{2\lambda B_{m,k}^{(m,k)}}{\rho} \right) F_{m,k}$$

$$- \frac{2}{\rho} \sum_{n=k}^{\infty}{}' A_n^{(m,k)} F_{n,k} + \frac{2\lambda}{\rho} \sum_{n=0}^{\infty}{}' \sum_{\ell=0}^{n}{}' B_{n,\ell}^{(m,k)} F_{n,\ell}$$

(13b)

where

$$\gamma_m = 4m(m+2) + \frac{15}{4}$$

and where the prime on the sums mean the terms with n=m, l=k are to be omitted.

Bartlett then appealed to the work of Pierce[96] to get a solution to this set of coupled equations. Pierce's work only concerned a finite set of coupled equations, not an infinite set such as this one and Bartlett suggests that solutions of this infinite problem could be found as the limit of a finite system. Actually the error made is more basic than this. Rather than go through the rather lengthy procedure that Bartlett applied to this set of equations, the same technique will be applied to a much simpler equation whose complete solution is known. It will then be obvious that the technique Bartlett used fails, even in this simple case, to reproduce the true solutions. The failure in the more complicated case then follows.

Consider the simple second order ordinary differential equation

$$\left(x^2 \frac{d^2}{dx^2} - 2 \right) y = 0 \ . \tag{14}$$

The general solution of this equation is

$$y = a_0 x^2 + \frac{a_1}{x} \ . \tag{15}$$

Now let

$$z = \frac{dy}{dx} \ .$$

The second order equation given by equation (14) is then equivalent to the simultaneous first order equations

$$\frac{dy}{dx} = z \ , \tag{16a}$$

$$\frac{dz}{dx} = \frac{2y}{x^2} \ . \tag{16b}$$

The technique which Bartlett used consists in

1. Assuming

$$y = \sum_{i=1}^{\infty} y_i \ , \tag{17}$$

$$z = \sum_{i=1}^{\infty} z_i \ ,$$

2. Solving the equations

$$\frac{dy_1}{dx} = \frac{dz_1}{dx} = 0 , \tag{18a}$$

$$\frac{dy_n}{dx} = z_{n-1} , \quad n = 2,3,4,\ldots \tag{18b}$$

$$\frac{dz_n}{dx} = \frac{2}{x^2} y_{n-1}, \quad n = 2,3,4,\ldots \tag{18c}$$

successively.

In a more general case than equation (16) the method is easily characterized by a matrix representation. Suppose the equation to be solved is

$$\frac{d}{dx} Y = A Y \tag{19}$$

where Y is a column vector of n unknowns and A is an n x n matrix of known coefficients. Partition A into two parts

$$A = B + C \tag{20}$$

where B is an n x n diagonal matrix and C is an n x n matrix with zero diagonal. Assume

$$\underline{Y} = \sum_{i=1}^{\infty} \underline{Y}_i \tag{21}$$

where the $\underline{Y}_i$ are again $n \times 1$ column vectors, and solve equation (19) by the recursive scheme

$$\frac{d}{dx} \underline{Y}_i = \underline{\underline{B}} \cdot \underline{Y}_i + \underline{\underline{C}} \cdot \underline{Y}_{i-1}, \quad i = 1, 2, 3, \cdots \tag{22}$$

with

$$\underline{Y}_0 \equiv \underline{0} .$$

Carrying out seven iterations of the above scheme leads to the result (See equation (17))

$$y = c_0 \left(1 - 14 \log x - 6 (\log x)^2 - \frac{4}{3} (\log x)^3 + \cdots \right)$$
$$+ c_1 x \left(1 - \frac{6}{7} \log x + \frac{2}{7} (\log x)^2 + \cdots \right). \tag{23}$$

The logarithmic terms that have appeared in this solution should not "really" be there in the sense that the solution, equation (15), does not possess this type of singularity. Of course, the logarithmic terms generated by this technique may be "trying" to converge to the true solution when written as

$$\frac{1}{X} = exp(-\log X) = 1 - \log X + \frac{1}{2}(\log X)^2 + \cdots; \quad (24)$$

However, it's clear that the infinite sum, equation (17), would at least have to be summed to yield the correct form of the solution.

Using this same technique on the infinite set of equations, equation (13), Bartlett concluded that the solution contains logarithmic terms in ρ . That this conclusion of Bartlett's is invalid is clear.

Appendix G. The Properties of $\square^*$

The operator $\square^*$ is the Laplacian on the four-dimensional sphere[66]. In general it is defined as

$$\square^* = \frac{1}{\sin^2\alpha}\left(\frac{\partial}{\partial\alpha}\sin^2\alpha\frac{\partial}{\partial\alpha} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right) \qquad (1)$$

For this problem, a physical meaning is attached only to solutions independent of the angle φ.

The eigenfunctions of the operator $\square^*$ may be called hyper-spherical harmonics and are well known[97]. The equation

$$\square^*\phi = \lambda\phi \qquad (2)$$

possesses solutions that are finite, single-valued and continuous everywhere on the four-dimensional unit sphere $(0 \leq \alpha \leq \pi, 0 \leq \theta \leq \pi, 0 \leq \varphi \leq 2\pi$) only if λ takes the values

$$\lambda = -n(n+2) \qquad (3)$$

where

$$n = 0, 1, 2, \cdots .$$

To every integral value of n there correspond n + 1 eigen-
functions independent of φ . These functions may be written

$$\phi = Z_{m\ell}(\alpha, \theta) = \sqrt{\frac{2\ell+1}{\pi}}\ \Pi_{m\ell}(\alpha)\ P_\ell(\cos\theta) \quad (4)$$

where P_ℓ is a Legendre polynomial and $\Pi_{m,\ell}$ is a Gegenbauer
polynomial that may be represented either in the form of an integral

$$\Pi_{m\ell}(\alpha) = \frac{N_{m\ell}}{(\sin\alpha)^{\ell+1}} \int_0^\alpha \cos(n+1)\beta\ \frac{(\cos\beta - \cos\alpha)^\ell}{\ell!}d\beta \quad (5)$$

or else in the form of a derivative

$$\Pi_{m\ell}(\alpha) = \frac{(\sin\alpha)^\ell}{N_{m\ell}}\ \frac{d^{\ell+1}\cos(n+1)\alpha}{d(\cos\alpha)^{\ell+1}} \quad (6)$$

where

$$N_{m\ell} = (n+1)^2\left((n+1)^2-1\right)\cdots\left((n+1)^2-\ell^2\right). \quad (7)$$

For a given n, ℓ takes the values

$$\ell = 0, 1, 2, \cdots, n. \quad (8)$$

The functions $\Pi_{m,\ell}$ are normalized in the following way

$$\int_0^\pi \Pi_{m,\ell}^2(\alpha)\ \sin^2\alpha\ d\alpha = \frac{\pi}{2}. \quad (9)$$

The following special formula holds

$$\Pi_{n,0}(\alpha) = \frac{\sin(n+1)\alpha}{\sin\alpha} \, . \qquad (10)$$

The $Z_{n\ell}$ are an orthonormal set in the following sense

$$\int_0^\pi d\alpha \int_0^\pi d\theta \, \sin^2\alpha \, \sin\theta \, Z_{n,\ell} Z_{m,k} = \delta_{n,m} \delta_{\ell,k} \qquad (11)$$

where the $\delta_{n,m}$ are the Dirac delta functions.

The following is a list of the first few hyperspherical harmonics.

$$Z_{0,0} = \left(\frac{1}{\pi}\right)^{1/2}, \qquad (12)$$

$$Z_{1,0} = \left(\frac{12}{\pi}\right)^{1/2} \cos\alpha, \qquad (13)$$

$$Z_{1,1} = \left(\frac{4}{\pi}\right)^{1/2} \sin\alpha \, \cos\theta, \qquad (14)$$

$$Z_{2,0} = \left(\frac{1}{\pi}\right)^{1/2} (4\cos^2\alpha - 1), \tag{15}$$

$$Z_{2,1} = \left(\frac{6}{\pi}\right)^{1/2} \sin 2\alpha \cos\theta, \tag{16}$$

$$Z_{2,2} = \left(\frac{1}{2\pi}\right)^{1/2} \sin^2\alpha (3\cos^2\theta - 1). \tag{17}$$

Appendix H - Boundary Condition Due to Hermiticity of the Kinetic Energy in Hylleraas Coordinates

As an illustration of the technique used to find appropriate boundary conditions on wave functions when using coordinates which do not have independent ranges a detailed study is made here of the s, t, u system.

Since the domain is determined by the kinetic energy alone[64], when the potential is coulombic, the requirement of hermiticity of the hamiltonian leads to the relation

$$\langle \Phi, (\nabla_1^2 + \nabla_2^2) \Psi \rangle = \langle (\nabla_1^2 + \nabla_2^2) \Phi, \Psi \rangle \tag{1}$$

for all Φ and Ψ in the domain, $\mathcal{D}_0$, of the hamiltonian. The vanishing of the surface terms produced when the left hand side of (1) is integrated by parts to produce the right hand side corresponds to the vanishing of the bilinear concomitant or conjunct of Φ and Ψ on the bounding surfaces of the coordinate system.

Appendix B gives the form of $\nabla_1^2 + \nabla_2^2$ and of the integration over all space to be used when employing the coordinates s,t,u,

$$\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) = \frac{1}{\mu}\frac{\partial^2}{\partial\mu^2}\mu \;+\; \frac{1}{s^2-t^2}\frac{\partial^2}{\partial s^2}(s^2-t^2)$$

$$+\; \frac{1}{s^2-t^2}\frac{\partial^2}{\partial t^2}(s^2-t^2) \;+\; \frac{2t(s^2-\mu^2)}{\mu(s^2-t^2)}\frac{\partial^2}{\partial\mu\partial t}$$

$$+\; \frac{2s(\mu^2-t^2)}{\mu(s^2-t^2)}\frac{\partial^2}{\partial\mu\partial s}\Big) \tag{2}$$

$$\frac{\langle\psi,\phi\rangle}{\pi^2} = \int_0^\infty ds\int_{-s}^{+s}dt\int_{|t|}^{s}d\mu\;\mu(s^2-t^2)\,\psi^*\phi$$

$$= \int_0^\infty d\mu\int_\mu^\infty ds\int_{-\mu}^{+\mu}dt\;\mu(s^2-t^2)\,\psi^*\phi. \tag{3}$$

In what follows all functions will be taken to be real and since the ground state is of interest here all functions will be assumed to be even in the variable t . The factor $2\pi^2$ in front of the integrals will be ignored since it has no function in this type of analysis. Write equation (2) as

$$\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) = P_1 + P_2 + P_3 + P_4 + P_5 \tag{4}$$

where

$$P_1 = \frac{1}{\mu} \frac{\partial^2}{\partial \mu^2} \mu ,$$

(5a)

$$P_2 = \frac{1}{s^2 - t^2} \frac{\partial^2}{\partial s^2} (s^2 - t^2) ,$$

(5b)

$$P_3 = \frac{1}{s^2 - t^2} \frac{\partial^2}{\partial t^2} (s^2 - t^2) ,$$

(5c)

$$P_4 = \frac{2t(s^2 - \mu^2)}{\mu(s^2 - t^2)} \frac{\partial^2}{\partial \mu \partial t} ,$$

(5d)

and

$$P_5 = \frac{2s(\mu^2 - t^2)}{\mu(s^2 - t^2)} \frac{\partial^2}{\partial \mu \partial s} .$$

(5e)

Consider the term

$$\langle \Phi, P_1 \Psi \rangle = \int_0^\infty ds \int_0^S dt \int_t^S (s^2 - t^2) \, \Phi \, \frac{\partial^2 (\mu \Psi)}{\partial \mu^2} \, d\mu \,. \tag{6}$$

Integrate by parts once

$$\langle \Phi, P_1 \Psi \rangle = \int_0^\infty ds \int_0^S dt \, (s^2 - t^2) \left(\Phi \frac{\partial}{\partial \mu} (\mu \Psi) \right) \Big|_t^S$$

$$- \int_0^\infty ds \int_0^S dt \, (s^2 - t^2) \int_t^S \left(\frac{\partial \Phi}{\partial \mu} \right) \frac{\partial}{\partial \mu} (\mu \Psi) \, d\mu \tag{7}$$

and then a second time

$$\langle \Phi, P_1 \Psi \rangle = \int_0^\infty ds \int_0^S dt \, (s^2 - t^2) \left(\Phi \frac{\partial}{\partial \mu} (\mu \Psi) - \mu \Psi \frac{\partial \Phi}{\partial \mu} \right) \Big|_t^S$$

$$+ \int_0^\infty ds \int_0^S dt \, (s^2 - t^2) \int_t^S \mu \Psi \, \frac{\partial^2 \Phi}{\partial \mu^2} \, d\mu \,. \tag{8}$$

Repeat this for $P_2 - P_5$:

$$\langle \Phi, P_2 \Psi \rangle = \int_0^\infty \mu \, d\mu \int_0^\mu dt \int_\mu^\infty \Phi \, \frac{\partial^2}{\partial s^2} [(s^2 - t^2) \Psi] \, ds \tag{9}$$

$$\langle \Phi, P_2 \Psi \rangle = \int_0^\infty u\, du \int_0^\mu dt \left(\Phi \frac{\partial}{\partial s}[(s^2-t^2)\Psi] \right)\Big|_s\Big|_\mu^\infty$$

$$- \int_0^\infty u\, du \int_0^\mu dt \int_\mu^\infty \frac{\partial \Phi}{\partial s}\ \frac{\partial}{\partial s}[(s^2-t^2)\Psi]\, ds \tag{10}$$

$$= \int_0^\infty u\, du \int_0^\mu dt \left(\Phi \frac{\partial}{\partial s}[(s^2-t^2)\Psi] - (s^2-t^2)\Psi \frac{\partial \Phi}{\partial s} \right)\Big|_s\Big|_\mu^\infty$$

$$+ \int_0^\infty u\, du \int_0^\mu dt \int_\mu^\infty ds\ (s^2-t^2)\Psi \frac{\partial^2 \Phi}{\partial s^2} . \tag{11}$$

$$\langle \Phi, P_3 \Psi \rangle = \int_0^\infty u\, du \int_\mu^\infty ds \int_0^\mu \Phi\ \frac{\partial^2}{\partial t^2}[(s^2-t^2)\Psi]\, dt \tag{12}$$

$$= \int_0^\infty u\, du \int_\mu^\infty ds \left(\Phi \frac{\partial}{\partial t}[(s^2-t^2)\Psi] - (s^2-t^2)\Psi \frac{\partial \Phi}{\partial t} \right)\Big|_t\Big|_0^\mu$$

$$+ \int_0^\infty u\, du \int_\mu^\infty ds \int_0^\mu dt\ (s^2-t^2)\Psi \frac{\partial^2 \Phi}{\partial t^2} . \tag{13}$$

$$\langle \Phi, P_4 \Psi \rangle = 2\int_0^\infty ds \int_0^s dt \int_t^s du\ t\ (s^2-u^2)\Phi \frac{\partial^2 \Psi}{\partial u \partial t} \tag{14}$$

$$\langle \Phi, P_4 \Psi \rangle = 2 \int_0^\infty ds \int_0^s dt \; t \, (s^2 - \mu^2) \, \bar{\Phi} \, \frac{\partial \Psi}{\partial t} \Big|_{\mu}^{s} \Big|_t$$

$$- 2 \int_0^\infty d\mu \int_\mu^\infty ds \int_0^\mu dt \left[t (s^2 - \mu^2) \frac{\partial \bar{\Phi}}{\partial \mu} - 2 \mu t \bar{\Phi} \right] \frac{\partial \Psi}{\partial t}$$

$$\tag{15}$$

$$= 2 \int_0^\infty ds \int_0^s dt \; t \, (s^2 - \mu^2) \, \bar{\Phi} \, \frac{\partial \Psi}{\partial t} \Big|_{\mu}^{s} \Big|_t$$

$$- 2 \int_0^\infty d\mu \int_\mu^\infty ds \; \Psi \left[t (s^2 - \mu^2) \frac{\partial \bar{\Phi}}{\partial \mu} - 2 \mu t \bar{\Phi} \right] \Big|_{\mu} \Big|_{t=0}^{\mu}$$

$$+ 2 \int_0^\infty d\mu \int_\mu^\infty ds \int_0^\mu dt \left[\Psi (s^2 - \mu^2) \frac{\partial \bar{\Phi}}{\partial \mu} \right.$$

$$- 2 \mu \Psi \bar{\Phi} + t (s^2 - \mu^2) \Psi \frac{\partial^2 \bar{\Phi}}{\partial \mu \partial t}$$

$$\left. - 2 \mu t \, \Psi \, \frac{\partial \bar{\Phi}}{\partial t} \right] .$$

$$\tag{16}$$

$$\langle \Phi, P_s \Psi \rangle = 2 \int_0^\infty ds \int_0^s dt \int_t^s du \; s(u^2 - t^2) \, \bar{\Phi} \, \frac{\partial^2 \Psi}{\partial u \partial s}$$

$$\text{(17)}$$

$$= 2 \int_0^\infty ds \int_0^s dt \left(s(u^2 - t^2) \, \bar{\Phi} \, \frac{\partial \Psi}{\partial s} \right)_u \Big|_t^s$$

$$- 2 \int_0^\infty du \int_0^u dt \int_u^\infty ds \left[s(u^2 - t^2) \frac{\partial \bar{\Phi}}{\partial u} + 2su \bar{\Phi} \right] \frac{\partial \Psi}{\partial s}$$

$$= 2 \int_0^\infty ds \int_0^s dt \left(s(u^2 - t^2) \, \bar{\Phi} \, \frac{\partial \Psi}{\partial s} \right)_u \Big|_t^s$$

$$- 2 \int_0^\infty du \int_0^u dt \; \Psi \left(s(u^2 - t^2) \frac{\partial \bar{\Phi}}{\partial u} + 2su \bar{\Phi} \right) \Big|_s \Big|_u^\infty$$

$$+ 2 \int_0^\infty du \int_0^u dt \int_u^\infty ds \; \Psi \left[(u^2 - t^2) \frac{\partial \bar{\Phi}}{\partial u} \right.$$

$$+ 2u \bar{\Phi} + s(u^2 - t^2) \frac{\partial^2 \bar{\Phi}}{\partial u \partial s}$$

$$\left. + 2su \frac{\partial \bar{\Phi}}{\partial s} \right] \qquad \text{(18)}$$

Now add equations (8), (11), (13), (16) and (18) to get

$$\frac{1}{2}\langle \bar{\Phi}, (\nabla_1^2 + \nabla_2^2)\Psi\rangle = \frac{1}{2}\langle (\nabla_1^2 + \nabla_2^2)\bar{\Phi}, \Psi\rangle$$

$$+ \int_0^\infty ds \int_0^s dt \left[(s^2 - t^2)\bar{\Phi}\Psi + 2t(s^2 - u^2)\bar{\Phi}\frac{\partial \Psi}{\partial t} \right.$$

$$\left. + 2s(u^2 - t^2)\bar{\Phi}\frac{\partial \Psi}{\partial s} + u(s^2 - t^2)\left(\bar{\Phi}\frac{\partial \Psi}{\partial u} - \Psi\frac{\partial \bar{\Phi}}{\partial u}\right)\right]\Big|_u^s\Big|_t$$

$$+ \int_0^\infty du \int_0^u dt \left[-2su\Psi\bar{\Phi} - 2s(u^2 - t^2)\Psi\frac{\partial \bar{\Phi}}{\partial u} \right.$$

$$\left. + u(s^2 - t^2)\left(\bar{\Phi}\frac{\partial \Psi}{\partial s} - \Psi\frac{\partial \bar{\Phi}}{\partial s}\right)\right]_s\Big|_u^\infty$$

$$+ \int_0^\infty ds \int_0^s du \left[2ut\,\bar{\Phi}\Psi - 2t(s^2 - u^2)\Psi\frac{\partial \bar{\Phi}}{\partial u} \right.$$

$$\left. + u(s^2 - t^2)\left(\bar{\Phi}\frac{\partial \Psi}{\partial t} - \Psi\frac{\partial \bar{\Phi}}{\partial t}\right)\right]_t\Big|_0^u.$$

$$(19)$$

This may be put in a more symmetrical form by observing that the starting point could have been the right side of equation (1) instead of the left side. This would have merely changed the roles of Φ and Ψ . Adding the two forms yields

$$\langle \Phi, (\nabla_1^2 + \nabla_2^2)\Psi \rangle - \langle (\nabla_1^2 + \nabla_2^2)\Phi, \Psi \rangle$$

$$= 2\int_0^\infty ds \int_0^S dt \left[t(s^2 - u^2)\left(\Phi\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Phi}{\partial t}\right) \right.$$

$$+ S(u^2 - t^2)\left(\Phi\frac{\partial\Psi}{\partial s} - \Psi\frac{\partial\Phi}{\partial s}\right)$$

$$+ \left. u(s^2 - t^2)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right] \Big|_{u|t}^{S}$$

$$+ 2\int_0^\infty du \int_0^u dt \left[u(s^2 - t^2)\left(\Phi\frac{\partial\Psi}{\partial s} - \Psi\frac{\partial\Phi}{\partial s}\right) \right.$$

$$+ \left. S(u^2 - t^2)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right] \Big|_{S|u}^{\infty}$$

$$+ 2\int_0^\infty ds \int_0^S du \left[u(s^2 - t^2)\left(\Phi\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Phi}{\partial t}\right) \right.$$

$$+ \left. t(s^2 - u^2)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right] \Big|_{t|0}^{u}$$

(20)

Delta functions may now be inserted to denote the boundary terms to give

$$\langle \Phi, (\nabla_1^2 + \nabla_2^2)\Psi \rangle - \langle (\nabla_1^2 + \nabla_2^2)\Phi, \Psi \rangle$$

$$= 2\int_0^\infty ds \int_0^S dt \int_t^S du \left[\delta(s-u)\left\{ t(s^2-u^2)\left(\Phi\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Phi}{\partial t}\right) \right.\right.$$

$$- (s-u)(su+t^2)\left(\Phi\frac{\partial\Psi}{\partial s} - \Psi\frac{\partial\Phi}{\partial s}\right)$$

$$\left. + (s-u)(su+t^2)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right\}$$

$$+ \delta(u-t)\left\{ -s(u^2-t^2)\left(\Phi\frac{\partial\Psi}{\partial s} - \Psi\frac{\partial\Phi}{\partial s}\right) \right.$$

$$+ (u-t)(s^2+ut)\left(\Phi\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Phi}{\partial t}\right)$$

$$\left. - (u-t)(s^2+ut)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right\}$$

$$+ \delta(s-\infty)\left\{ u(s^2-t^2)\left(\Phi\frac{\partial\Psi}{\partial s} - \Psi\frac{\partial\Phi}{\partial s}\right) \right.$$

$$\left. + s(u^2-t^2)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right\}$$

$$- \delta(t)\left\{ u(s^2-t^2)\left(\Phi\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Phi}{\partial t}\right) \right.$$

$$\left.\left. + t(s^2-u^2)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right\}\right] .$$

(21)

Under the assumption that Ψ and Φ are even in t , the last term vanishes if there are no negative powers of t (which are excluded by square-integrability). The second to last term vanishes if Ψ and Φ behave properly at $s = \infty$ as they must if they are square-integrable. This leaves two terms, one on the surface s = u and the other on the surface u = t . These must vanish for Φ and Ψ to belong to $\mathcal{D}_0$, the domain of the hamiltonian. This requires

$$\lim_{u \to s} (s-u)\left[t(s+u)\left(\Phi\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Phi}{\partial t}\right) \right.$$

$$- (su+t^2)\left(\Phi\frac{\partial\Psi}{\partial s} - \Psi\frac{\partial\Phi}{\partial s}\right)$$

$$\left. + (su+t^2)\left(\Phi\frac{\partial\Psi}{\partial u} - \Psi\frac{\partial\Phi}{\partial u}\right)\right] = 0$$

$$\text{all } s, t \qquad (22)$$

and

$$\lim_{\mu \to t} (\mu - t) \left[S(\mu + t) \left(\bar{\Phi} \frac{\partial \Psi}{\partial s} - \Psi \frac{\partial \bar{\Phi}}{\partial s} \right) \right.$$

$$- (s^2 + \mu t) \left(\bar{\Phi} \frac{\partial \Psi}{\partial t} - \Psi \frac{\partial \bar{\Phi}}{\partial t} \right)$$

$$\left. + (s^2 + \mu t) \left(\bar{\Phi} \frac{\partial \Psi}{\partial \mu} - \Psi \frac{\partial \bar{\Phi}}{\partial \mu} \right) \right] = 0$$

$$\text{all } s, t$$

$$(23)$$

Necessary requirements that any wave function must satisfy are that the above be true for Ψ = wave function considered, $\bar{\Phi}$ = some function known to be in $\mathcal{D}_0$. This requirement becomes sufficient only with $\bar{\Phi}$ being any arbitrary function in $\mathcal{D}_0$. A class of functions in $\mathcal{D}_0$ is given by

$$\tilde{\bar{\Phi}} = exp\left(- \frac{\alpha}{2} (s^2 + t^2)\right), \quad \alpha > 0 \qquad (24)$$

since this is equivalent to a subspace of the Hermite orthogonal functions[64]. Using this for $\bar{\Phi}$ in (22) and (23) leads to

$$\widetilde{\Phi} \lim_{\mu \to S} (S-\mu)\left[(S\mu+t^2)\left(\frac{\partial \Psi}{\partial \mu} - \frac{\partial \Psi}{\partial S} - \alpha S \Psi\right)\right.$$

$$\left. + t(S+\mu)\left(\frac{\partial \Psi}{\partial t} + \alpha t \Psi\right)\right] = 0,$$

$$(25)$$

$$\widetilde{\Phi} \lim_{\mu \to t} (\mu-t)\left/\left(S^2+\mu t\right)\left(\frac{\partial \Psi}{\partial \mu} - \frac{\partial \Psi}{\partial t} - \alpha t \Psi\right)\right.$$

$$\left. + S(\mu+t)\left(\frac{\partial \Psi}{\partial S} + \alpha S \Psi\right)\right] = 0.$$

As stated before, equations (25) and (26) certainly must hold for any acceptable Ψ , but these equations are not sufficient since $\widetilde{\Phi}$ is not the most general type of function in $\mathcal{A}_0$.

Appendix I. The Difference Between Formal Solutions and Actual
Solutions

Since there may be some confusion as to the meaning of the
statement that a certain function is a formal solution to an
equation but not an actual solution, this appendix will present
a simple example of a formal solution in the hopes of some
clarification.

Consider the equation for ψ_1

$$(H_0 - \epsilon_0)\psi_1 = \epsilon_1 \psi_0 \tag{1}$$

where

$$H_0 = -\frac{1}{2}\left(\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2} r_2 \right)$$
$$- \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2(\mathcal{D}+1)}{r_{12}}\frac{\partial}{\partial r_{12}} + 2\mathcal{D}' r_{12}\frac{\partial}{\partial r_{12}} \right)$$
$$- \frac{1}{r_1} - \frac{1}{r_2} \ ) \tag{2}$$

$$\epsilon_0 = -1, \tag{3}$$

$$\psi_0 = \pi^{-1} exp(-r_1 - r_2) \tag{4}$$

ϵ_1 is some constant and $\mathcal{D}$ and $\mathcal{D}'$ were defined by equation
(III.11). Immediately one would say this equation has a solution
only for $\epsilon_1 \cong 0$. To show this multiply both sides of
equation (1) by ψ_0 and integrate over all space. This leads to

the conclusion

$$\epsilon_1 \langle \psi_0, \psi_0 \rangle = \langle \psi_0, (H_0 - \epsilon_0)\psi_1 \rangle$$

$$= \langle (H_0 - \epsilon_0)\psi_0, \psi_1 \rangle$$

$$= 0 \tag{4}$$

since $H_0 - \epsilon_0$ is hermitian and $(H_0 - \epsilon_0)\psi_0 = 0$.

But the function

$$\psi_1 = \psi_c \frac{\epsilon_1}{2}\left[r_1 + r_2 - \frac{1}{2}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \log r_1 r_2 \right] \tag{5}$$

satisfies the equation in the sense that if the operations on the left-side of equation (1) are performed on ψ_1 given by (5) the right side is produced almost everywhere (the exception being the origin). ψ_1 given by equation (5) is only a formal solution of equation (1) by virtue of the fact that ψ_1 does not belong to the domain $\mathcal{D}_0$ on which H is hermitian.

The requirement that the kinetic energy be hermitian leads, in coordinates r_1, r_2, θ, to the requirement

$$\lim_{r_1 \to 0} r_1^2 \left(\Phi \frac{\partial \Psi}{\partial r_1} - \Psi \frac{\partial \Phi}{\partial r_1} \right) = 0. \tag{6}$$

Take $\Phi = exp\left(-\frac{\alpha r_1^2}{2}\right)$ which is certainly in the domain $\mathcal{D}_0$. Let $\Psi = \psi_1$ given by equation (5). Then

$$\lim_{r_1 \to 0} r_1^2 \left(\frac{\partial \psi_1}{\partial r_1} + \alpha r_1 \psi_1\right) = \frac{\epsilon_1}{4\pi} \qquad (7)$$

which is zero only for $\epsilon_1 = 0$. Thus a formal solution of an equation is one which yields an identity upon substitution into the equation, but which does not satisfy the boundary conditions associated with the particular problem.

In this respect it is worth noting that for the ground state of helium, no formal solution exists which contains only positive powers of the Hylleraas coordinates s,t,u due to an inconsistency which arises. A formal solution does exist for this equation if only positive powers of the variable $\rho = \sqrt{r_1^2 + r_2^2}$ are used, but no actual solution of the equation exists which is of this form due to an inability of this type of solution to satisfy certain boundary conditions.

Appendix J. Analytic Power Series Solution of the Schrödinger

Equation for the Helium Atom.

Integral Series Solution of the Schrödinger

Equation for the Helium Atom.

Erratum for Above.

PHYSICAL REVIEW

LETTERS

ANALYTIC POWER-SERIES SOLUTION OF THE SCHRÖDINGER EQUATION FOR THE HELIUM ATOM*

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The object of this Letter is to report the discovery of analytic solutions of the Schrödinger equation for the two-electron atom. In this preliminary communication we confine attention to the nonrelativistic Schrödinger equation[1] for a fixed nucleus of atomic number Z, and to the simplest S states (singlets or triplets) of the atom.

The Schrödinger equation in Z-reduced units (energy unit $= Z^2$ Hartree units, length unit $= Z$ Bohr radii) is

$$(\mathcal{K}_0 + \lambda r_{12}^{-1} - E)\psi = 0, \tag{1}$$

where $\lambda = Z^{-1}$ and

$$\mathcal{K}_0 = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - r_1^{-1} - r_2^{-1}. \tag{2}$$

For S states the spatial wave function ψ depends only on three variables which we take to be r_1, r_2, and r_{12}, the interparticle distances. When operating on functions of these variables, the unperturbed Hamiltonian can be written

$$\mathcal{K}_0 = \mathcal{K}_0' - \left[\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{2\mathfrak{D}}{r_{12}}\frac{\partial}{\partial r_{12}} + 2\mathfrak{D}' r_{12}\frac{\partial}{\partial r_{12}}\right], \tag{3}$$

where

$$\mathcal{K}_0' = -\frac{1}{2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2}\right] - r_1^{-1} - r_2^{-1}, \tag{4}$$

and

$$\mathfrak{D} = \frac{1}{4}(r_1^2 - r_2^2)\left(\frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right),$$

$$\mathfrak{D}' = \frac{1}{4}\left(\frac{1}{r_1}\frac{\partial}{\partial r_1} + \frac{1}{r_2}\frac{\partial}{\partial r_2}\right). \tag{5}$$

We assume a solution in the form of a power series in r_{12}, starting with the arbitrary power σ:

$$\psi = \sum_{n=0}^{\infty} r_{12}^{\sigma+n}\varphi_n(r_1, r_2), \tag{6}$$

with coefficients φ_n which are functions of r_1 and r_2 to be determined. This is a somewhat more general form than that proposed by Hylleraas[2] or by Kinoshita.[3] In spirit it is similar to the approach of Pluvinage.[4] By substituting (6) into Eq. (1), and using the independence of the powers of r_{12} within the range ($|r_1 - r_2|, r_1 + r_2$) to equate the coefficients to 0, we find that we must take $\sigma = 0$. The remaining equations then become

$$(\mathfrak{D} + 1)\varphi_1 = \tfrac{1}{2}\lambda\varphi_0, \tag{7}$$

$$\left[\mathfrak{D} + \tfrac{1}{2}(n+1)\right]\varphi_n = \frac{\lambda}{2n}\varphi_{n-1}$$

$$+ \left[\frac{1}{2n}(\mathcal{K}_0' - E) + \left(\frac{2}{n} - 1\right)\mathfrak{D}'\right]\varphi_{n-2} \tag{8}$$

for $n = 2, 3, \cdots$. Hence if $\varphi_0(r_1, r_2)$ is known, all the higher functions φ_n can be obtained iteratively by inverting the operators on the left-hand sides of Eqs. (7) and (8). Further, since $\mathfrak{D}$ is a first-order partial differential operator, the inversion can be carried out analytically by a single integration.

The key problem at this point is the form of the starting function φ_0. When the coupling parameter λ goes to 0, ψ approaches the cor-

responding eigenfunction ψ_0 of the unperturbed Hamiltonian satisfying $(\mathcal{K}_0 - E_0)\psi_0 = 0$, whose form is known explicitly. If we limit discussion to the simplest S states, which correlate with the singly excited nondegenerate unperturbed configuration $(1s)(ns)$, then[5] $\psi_0 = \psi_0(r_1, r_2)$. Hence when $\lambda \rightarrow 0$, $\varphi_0 \rightarrow \psi_0$ and all the other φ_n vanish. In the absence of further information about φ_0, it seems likely that we can take $\varphi_0 = \psi_0$ for all λ (ignoring a normalization constant depending on λ). This result may be proved by a perturbation analysis in powers of λ, which is known to be valid if λ is small enough.[6] The first-order treatment,[7] which led to the present work, shows that the only term independent of r_{12} in the first-order wavefunction is some multiple of ψ_0; the same is true for the higher order wavefunctions. Therefore, provided the perturbation series converges for the value of $\lambda(=Z^{-1})$ of interest,[8] we can take $\varphi_0 = \psi_0$.

To carry out the integrations, Eqs. (7) and (8) are most naturally written in terms of coordinates introduced by Gronwall[9] and Fock,[10] $x = r_1^2 + r_2^2$ and $y = r_1^2 - r_2^2$, so that $\mathfrak{D} = y\partial/\partial y$, $\mathfrak{D}' = \partial/\partial x$. Integrating the first two equations with respect to y, we get

$$\varphi_1 = \tfrac{1}{2}\lambda \int_0^1 \psi_0(x, \alpha y)d\alpha, \qquad (9)$$

$$\varphi_2 = \tfrac{1}{4}\int_0^1 [\lambda^2(1-\alpha^{1/2}) + (E_0-E)\alpha^{1/2}]\psi_0(x, \alpha y)d\alpha, \qquad (10)$$

where α is a dummy integration variable. In terms of the Hylleraas variables $s = r_1 + r_2$ and $t = r_1 - r_2$, $\varphi_1(s, t)$ for the ground state $(\psi_0 = \pi^{-1}e^{-s})$ takes the form

$$\varphi_1 = \frac{1}{2}\lambda\psi_0 - \frac{\lambda t^2}{4\pi s}\int_0^1 (1-\beta)^{1/2}\exp[-(s^2+\beta t^2)^{1/2}]d\beta, \qquad (11)$$

and φ_2 is given by a similar type of expression. The next member φ_3 can also be reduced to a single integral over ψ_0 and its derivatives, and this is probably true for all the higher φ_n. The functions $\varphi_n(s, t)$ may be expanded in powers of t^2, and most terms are then found to involve inverse powers of s. The possibility of a formal solution of the Hylleraas type,[2] provided inverse powers of s are included, was pointed out by Kinoshita.[3] There are no signs of logarithmic terms[10-12] in x or s in the early members, in agreement with the conclusion of Kinoshita[13]; nor of fractional powers[14] of s in the t^2 expansions. Further details

will be given in a subsequent paper.

The above techniques also yield analytic solutions of the Schrödinger equations for the two-electron atom in the presence of a uniform electric field, and for the two-electron diatomic molecule, hydrogen.[15] The applications to arbitrary states of the two-electron atom and to the general three-body problem are being considered. It is interesting to note that in the case of the lithium atom, where interparticle coordinates can also be used, the obvious generalization of Eq. (6) to a triply infinite power series in r_{12}, r_{23}, and r_{31} leads to an inconsistency (of order λ^2) if only positive powers are allowed.

The practical weakness of the power-series solution (6) is that it almost certainly converges slowly. A more powerful approach leading to a more rapidly convergent analytic solution is proposed in the following Letter.[16]

*This research was supported by the National Aeronautics and Space Administration, Grant No. NsG-275-62.

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[3]T. Kinoshita, Phys. Rev. 105, 1490 (1957).

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[5]For S states correlating with doubly excited unperturbed configurations with principal quantum numbers n and n' $(n \le n')$, which are n-fold degenerate, $\psi_0(r_1, r_2, r_{12})$ is a polynomial of degree $n-1$ in r_{12}^2.

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INTEGRAL SERIES SOLUTION OF THE SCHRÖDINGER EQUATION FOR THE HELIUM ATOM*

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In the preceding Letter,[1] a method for obtaining analytic solutions of the nonrelativistic Schrödinger equation for the two-electron atom of infinite nuclear mass was described. The solution for the spatial wave function $\psi(r_1, r_2, r_{12})$ of the simplest type of S state can be written in the form of an infinite power series in the interelectron distance r_{12},

$$\psi = \mathbf{w}\psi_0 = \sum_{n=0}^{\infty} r_{12}{}^n \mathbf{w}_n \psi_0. \tag{1}$$

In this equation $\psi_0(r_1, r_2)$ is the corresponding eigenfunction of the unperturbed Hamiltonian $\mathcal{K}_0$ in which the electron repulsion term is absent, and the $\mathbf{w}_n$ are integrodifferential operators satisfying three-term recursion relations, which depend implicitly on the energy E. The eigenvalue can be found by multiplying the Schrödinger equation $(\mathcal{K}_0 + V)\psi = E\psi$ by ψ_0 and integrating to obtain

$$E = E_0 + \langle \psi_0, V\psi \rangle / \langle \psi_0, \psi \rangle, \tag{2}$$

and then solving this implicit equation for E iteratively.

The power series solution (1) has the theoretical advantage of being almost certainly uniformly convergent, as compared with the variational forms of Hylleraas[2] or Pekeris,[3] which are only convergent in the mean. However, it suffers from the practical disadvantage of almost certainly converging slowly for most configurations of the electrons. It is therefore necessary to sum at least some of the terms to obtain a potentially useful solution. The purpose of the present Letter is to describe an alternative approach which achieves such a summation implicitly, and which avoids the assumption of a power series form. In this preliminary communication, we shall merely sketch the method without attempt at rigor.

We partition[4] the Hamiltonian for the two-electron atom with atomic number Z into[5] $\mathcal{K} = \mathcal{K}' + \Lambda$ where, in Z-reduced atomic units (energy unit $= Z^2$ Hartree, length unit $= Z$ Bohr),

$$\mathcal{K}' = -\frac{1}{2}\left[\frac{\partial^2}{\partial r_1{}^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2{}^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2}\right]$$
$$-r_1{}^{-1} - r_2{}^{-1} + \lambda r_{12}{}^{-1}, \tag{3}$$

$$\Lambda = -\left[\frac{\partial}{\partial r_{12}} + \frac{2(1+\mathcal{D})}{r_{12}} + 2r_{12}\mathcal{D}'\right]\frac{\partial}{\partial r_{12}}, \tag{4}$$

with $\lambda = Z^{-1}$ and

$$\mathcal{D} = \frac{1}{4}(r_1{}^2 - r_2{}^2)\left(\frac{1}{r_1}\frac{\partial}{\partial r_1} - \frac{1}{r_2}\frac{\partial}{\partial r_2}\right),$$
$$\mathcal{D}' = \frac{1}{4}\left(\frac{1}{r_1}\frac{\partial}{\partial r_1} + \frac{1}{r_2}\frac{\partial}{\partial r_2}\right). \tag{5}$$

The Schrödinger equation $(\mathcal{K} - E)\psi = 0$ may then be written in the form

$$\Lambda\psi = (E - \mathcal{K}')\psi. \tag{6}$$

Let Λ^{-1} denote the inverse (Green's operator) of Λ in the subspace complementary to that of the functions φ satisfying the homogeneous equation $\Lambda\varphi = 0$. Then Eq. (6) can be rewritten as the integral-type equation

$$\psi = \varphi_0 + \Lambda^{-1}(E - \mathcal{K}')\psi, \tag{7}$$

where φ_0 is the appropriate solution of $\Lambda\varphi = 0$. Clearly, as $\lambda \to 0$, $\varphi_0 \to \psi_0$, and a perturbation analysis[1] proves that we can take $\varphi_0 = \psi_0$. In contrast to the reduced resolvent $(E_0 - \mathcal{K}_0)^{-1}$, the inverse Λ^{-1} can be realized explicitly as a double integral, by using the theory of characteristics of partial differential equations.[6] Thus, when operating on a function of the coordinates $x = r_1{}^2 + r_2{}^2$, $y = r_1{}^2 - r_2{}^2$, and $u = r_{12}$, the inhomogeneous part may be written in the form

$$\Lambda^{-1}f(x, y, u) = -\frac{1}{4}u^2 \int_0^1 \int_0^1 \alpha^{1/2} f(x - u^2(1-\alpha)\beta, y\alpha, u(\alpha\beta)^{1/2})d\alpha d\beta, \tag{8}$$

where α and β are dummy integration variables.

Assuming convergence, the solution of Eq. (7) can be written in a formally closed, wave operator

form

$$\psi = [1 - \Lambda^{-1}(E - \mathcal{3C}')]^{-1}\psi_0$$

$$= \{1 - [1 - \Lambda^{-1}(E - \mathcal{3C}')]^{-1}\Lambda^{-1}V\}\psi_0$$

$$= \mathcal{W}\psi_0, \qquad (9)$$

where $V = \lambda r_{12}^{-1}$. In practice, ψ has to be expanded as the infinite series

$$\psi = \psi_0 - \Lambda^{-1}V\psi_0 - \Lambda^{-1}(E - \mathcal{3C}')\Lambda^{-1}V\psi_0 - \cdots, \qquad (10)$$

where each term can be realized as a definite integral. By expanding each term in powers of r_{12} we recover the power series form (1). The eigenvalue can be found by substituting (10) into Eq. (2) and solving iteratively[7] for E.

The crucial practical question is: How rapidly does the integral series (10) converge? The only information on this point available at present is for the Hooke's law model atom,[8,9] in which the electrons are attracted to the nucleus by a parabolic potential well, but repel each other Coulombically. In this case the terms of Eq. (10) converge at least as rapidly as the successive orders of Rayleigh-Schrödinger perturbation theory in powers of λ. If this is also true for the actual two-electron atom it is highly satisfactory: The ground-state eigenvalue of helium is given to within 2 parts in 10^6 by the first six terms of the perturbation series.[10,11]

The Λ^{-1} technique can also be applied to the Schrödinger equation for the two-electron di-atomic molecule, hydrogen.[12] It is hoped it may be useful in the direct nonvariational solution of the pair equations of the Bethe-Goldstone type for many-electron atoms and diatomic molecules. Computations are in progress to find how rapidly Eq. (10) converges. In the event that convergence is too slow, it may be necessary to consider the series obtained by inverting $\Lambda + V - L$, where L is a number. This also appears to be possible explicitly,[13] but is considerably more complicated than the Λ^{-1} method outlined above.

[1]W. Byers Brown and R. J. White, preceding Letter [Phys. Rev. Letters 18, 1037 (1967)].

[2]E. A. Hylleraas, Z. Physik 54, 347 (1929).

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[4]We are using the term partition loosely in order to relate our approach to P. O. Löwdin, J. Math. Phys. 3, 969 (1962).

[5]The operator $\mathcal{3C}'$ is defined for fixed r_{12}, not fixed angle θ_{12} between $\vec{r}_1$ and $\vec{r}_2$. Neither $\mathcal{3C}'$ nor Λ is Hermitian with respect to functions belonging to the domain of $\mathcal{3C}$.

[6]R. Courant, Methods of Mathematical Physics (Interscience Publishers, Inc., New York, 1962), Vol. 2, p. 62.

[7]Note that, since Λ is not self-adjoint, the denominator of Eq. (2) cannot in general be set equal to unity. Furthermore, the bracketing theorem of Löwdin (Ref. 4), which is valid when $\mathcal{W}$ is the true Brillouin-Wigner wave operator, does not appear to hold when $\mathcal{W}$ is defined by Eq. (9).

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Erratum

This article is taken from Phys. Rev.

Letters 18, 1178 (1967).

ANALYTIC POWER SERIES SOLUTION OF THE
SCHRÖDINGER EQUATION FOR THE HELIUM
ATOM and INTEGRAL SERIES SOLUTION OF
THE SCHRÖDINGER EQUATION. W. Byers
Brown and R. J. White [Phys. Rev. Letters 18,
1037, 1039 (1967)].

The analytic solutions proposed in our Letters
can be expanded as power series $x^{1/2} = (r_1^2 + r_2^2)^{1/2}$.
Some years ago Bartlett[1] and more recently
Fock[2] proved that solutions of this form do not
exist, because they fail to satisfy the bound-
ary conditions required of functions belonging to
the domain in which the Hamiltonian $\mathcal{H}$ is self-
adjoint. The error in our treatment, which led
to us the conclusion that $\varphi_0 = \psi_0$, was to apply Ka-
to's theorem[3] to a function not belonging to the
domain of $\mathcal{H}$.

The form for ψ proposed by Fock[2] can be ex-
pressed as a power series[4] in r_{12}, as in Eq. (6)
of our first Letter. To complete our treatment
we have therefore to determine $\varphi_0(r_1, r_2)$ so that
ψ satisfies the proper boundary conditions. The
work of Bartlett[1] and Fock[2] shows that the cor-
rect φ_0 contains terms logarithmic in x.

[1]J. H. Bartlett, Phys. Rev. 51, 661 (1937).
[2]V. A. Fock, Izv. Akad. Nauk SSSR, Ser. Fiz. 18,
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Appendix K.   Bibliography on Ground State of the Two-Electron Atom

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Table 1

Selected Values of the Non-relativistic Ground State Energy of
the Helium Atom (Hartrees). Direct r_{ij} method.

Number of terms	-E	Comments
6	2.903 24	Hylleraas type[12]
3	2.903 265	exponential dependence on r_{12}[104]
10	2.903 639	H. M. Schwartz type[32]
20	2.903 718	Hylleraas type[105]
24	2.903 721 5	log terms[34]
31	2.903 721 59	H. M. Schwartz type[71]
39	2.903 722 5	Kinoshita type[36]
80	2.903 723 7	Kinoshita type[25]
42	2.903 724 21	Kinoshita type[67]
164	2.903 724 361 6	C. Schwartz type[33]
1078	2.903 724 375	Pekeris expansion[38]
189	2.903 724 377 032 6	Log terms and half-integral powers[3]

Table 2

Selected Values of the Non-relativistic Ground State Energy of the
Helium Atom (Hartrees). Multi-configurational Expansion.

Number of terms	-E	Comments
1	2.861 680	Hartree-Fock[17]
6	2.877 995	DODS[106]
21	2.878 970	S limit[107] ($\ell = 0$ terms only in P_ℓ expansion)
20	2.903 22	Natural Orbital type[23]
680	2.903 442 635	Incomplete minimization[108]

Table 3

Lower Bounds to the Non-relativistic Energy of the $1s^2$ ^1S State
of Helium (Hartrees).

Number of Parameters	$-E_L$	Technique
39	2.911 006	Weinstein Method[99]
10	2.910 16	Stevenson Method[90]
10	2.905 9	Intermediate Hamiltonian[100]
10	2.905 92	Bracketing Technique[95]
18	2.905 496	Temple Method[101]
18	2.903 9	Bracketing Technique[27]
39	2.903 877 7	Temple Method[94]
80	2.903 746 7	Modified Stevenson Method[25]
1078	2.903 724 375	Temple Method[26]

Table 4
Energy Coefficients in Z^{-1} Perturbation Expansion for the
Ground State of the Two-Electron Atom (Hartrees).

	Hylleraas[13]	Hylleraas-Midtdal[34]	Scherr-Knight[50]	Midtdal[47]
ϵ_0	-1.	-1.	-1.	-1.
ϵ_1	0.625	0.625	0.625	0.625
ϵ_2	-0.157 44	-0.157 657	-0.157 666 405	-0.157 666 428
ϵ_3		-0.008 535	0.008 698 991	0.008 699 029
ϵ_4		-0.000 34	-0.000 888 587	-0.000 888 705
ϵ_5		-0.000 82	-0.001 036 372	-0.001 036 374
ϵ_6		-0.002 44	-0.000 612 917	-0.000 612 932
ϵ_7			-0.000 372 187	-0.000 372 184
ϵ_8			-0.000 242 872	-0.000 242 874
ϵ_9			-0.000 165 651	-0.000 165 662
ϵ_{10}			-0.000 116 157	-0.000 116 179
ϵ_{11}			-0.000 083 281	-0.000 083 302
ϵ_{12}			-0.000 060 866	-0.000 060 881
ϵ_{13}			-0.000 045 213	-0.000 045 232
ϵ_{14}				-0.000 034 080
ϵ_{15}				-0.000 025 993
ϵ_{16}				-0.000 020 034
ϵ_{17}				-0.000 015 586
ϵ_{18}				-0.000 012 226
ϵ_{19}				-0.000 009 661
ϵ_{20}				-0.000 007 686
ϵ_{21}				-0.000 006 152

Table 5

Energy Coefficients for the Ground State of Helium in a Perturbation
Expansion with the Hartree-Fock Wave Function as the
Zeroth-Order Function (Hartrees).

Order	Energy[56]
$\epsilon_0 + \epsilon_1$	-2.861 67
ϵ_2	-0.037 25
ϵ_3	-0.003 77
ϵ_4	-0.000 85
ϵ_5	-0.000 16

Table 6

The Contributions of the Various Partial Waves to the Second
Order Energy (in Z^{-1} Perturbation Theory) of the
Ground State of Helium (Hartrees).

ℓ	Byron and Joachain [56]	Scherr and Knight [102]	Schwartz [103]
0	+0.125 334	0.125 331 98	0.125 27
1	+0.026 495	0.026 446 09	0.026 3
2	0.003 906	0.003 612 37	0.003 4
3	0.001 077		0.000 68
4	0.000 405		0.000 09
5	0.000 183		
6	0.000 094		
7	0.000 053		
8	0.000 032		
9	0.000 021		
10	0.000 014		
11	0.000 042		

Table 7

Energy Coefficients in Z^{-1} Expansion for the Models Studied (hartrees)

	Hooke Atom	Delta Atom	Actual Atom[47]
ϵ_0	3	-1	-1
ϵ_1	0.797 88	0.5	0.625
ϵ_2	-0.077 891	-0.162 79	-0.157 66
ϵ_3	0.011 253	0.013 989	0.008 699 0
ϵ_4	-0.001 148 9		-0.000 888 71
ϵ_5	0.000 001 268		-0.001 036 3
ϵ_6	0.000 026 767		-0.000 612 93
ϵ_7	-0.000 004 655		-0.000 372 18
ϵ_8	-0.000 000 079		-0.000 242 87
ϵ_9	0.000 000 192		-0.000 165 66
ϵ_{10}	-0.000 000 034		-0.000 116 18
ϵ_2^{corr}	-0.049 703	-0.079 46	-0.046 663
ϵ_3^{corr}	0.093 69	0.013 989	0.009 753 9

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Addendum: The 1/Z Perturbation Theory of the Hooke's

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